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EXPERIMENTS WITH UNDERGROUND ULTRA-HIGH-FREQUENCY ANTENNA FOR AIRPLANE LANDING BEAM

By Harry Diamond and Francis W. Dunmore

ABSTRACT

Experiments are described on the electrical properties of an ultra-high-frequency transmitting antenna operating very near to and below the ground surface. The work was done with the purpose of locating the landing beam in the center of an airport in order to secure a steeper approach path and to provide for landing service for different wind directions. The effect of the proximity of the ground to the transmitting antenna upon the low-angle distribution of energy in the radiated field and upon the polarization of the field is described. An approximate mathematical analysis is given of the mechanism of setting up a landing path when the transmitting antenna is below the ground surface.

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I. INTRODUCTION

In the course of experiments with the radio landing beam [1] an investigation was made during 1933–34 on the operation of an ultra-high-frequency transmitting antenna very near to and below the ground surface. The work was done with the purpose of locating the landing-beam antenna in the center of a landing field. In this location the approach path becomes steeper for a given point of contact of the landing airplane with the airport surface and thereby permits full utilization of long runways without requiring a very flat approach to the airport. A further advantage of this location is that landing-beam service may be provided for all directions of approach to the airport to meet varying wind conditions. The investigation led to what appears to be a practicable solution of locating the landing-beam antenna in the center of an airport. In addition, a number of interesting phenomena on the effects of the proximity of the ground upon the transmitted wave were observed and are reported in this paper.

[1] H. Diamond and F. W. Dunmore, *A Radiobeacon and receiving system for blind landing of aircraft.* BS J. Research **5**, 897–931 (1930) RP238. Proc. Inst. Radio Engrs. **19**, 585–626 (1931). H. Diamond, *Performance tests of radio systems of landing aids.* BS J. Research **11**, 463–490 (1933) RP602. Proc. Inst. Radio Engrs. **22**, 120–121 (1934).

II. INCREASED STEEPNESS OF APPROACH

That a steeper approach path is obtainable by locating the transmitting antenna at the center of the field is clearly evident from figure 1. Graph *A* is the theoretical landing path with the landing-beam transmitter located at the far edge of the field and the sensitivity of the airplane receiver adjusted so that the point of contact of the landing airplane with the airport surface is at a point 1,000 ft on the approach side of the center of the field. Graph *B* shows the theoretical landing path corresponding to the same point of contact, but with the transmitter at the center of the field. The length of airport runway in this illustration is assumed 5,000 ft, and the height of the airplane receiving antenna 10 ft. It is of interest to note that the obstacles in the approach would prevent the possibility of following path *A*, the airplane clearing the edge of the airport by only 10 ft (the difference between the height of the landing path at that point (20 ft) and the height of the receiving antenna above the bottom of the landing gear). In case of path *B*, the steepness of approach is more normal and the airplane clears the edge of the field by 53 ft.

Not only does the center-of-field location provide a steeper approach path for a given point of contact, but also it affords considerable flexibility for varying the steepness of approach without appreciable change in the point of contact. Thus the clearance at the approach end of the field may be doubled by moving the point of contact only 250 ft toward the center of the field. With the transmitter located at the far edge of the field, this clearance would require moving the point of contact by 2,000 ft, that is, to within 1,500 ft of the far edge of the field, thereby seriously reducing the length of runway available for coming to a stop.

III. TESTS WITH TRANSMITTING ANTENNA AT SMALL DISTANCES ABOVE THE GROUND SURFACE

Because of its location in the center of an airport, the choice of the transmitting antenna to be employed was necessarily restricted to the simplest possible type. Accordingly, a horizontal half-wave transmitting antenna was adopted and was used throughout the tests.

The use of a simple half-wave antenna in place of the directive antenna array previously employed for setting up a landing path led to a consideration of whether the transmitter power and receiver sensitivity employed were sufficient. Also, while optical theory showed that the slope of the landing path would be the same for both types of antennas, it was desired to determine the effect on the path of placing the transmitting antenna close to the ground surface. Tests were accordingly made to investigate these features.

The transmitter utilized two 500-w tubes in push-pull, operating at a frequency of 90,800 kc (3.3 m), and the half-wave antenna was fed from it by a short two-wire parallel-conductor transmission line. The transmitter was completely shielded and the transmission line properly terminated so that the radiation was confined to the antenna proper. The receiving equipment consisted of a detector and a two-stage audio amplifier fed by a parallel-conductor transmission line from a half-wave receiving antenna. The output of the receiver was rectified and applied to the landing beam indicator (a d-c microammeter). The receiver sensitivity corresponding to half-scale ("on

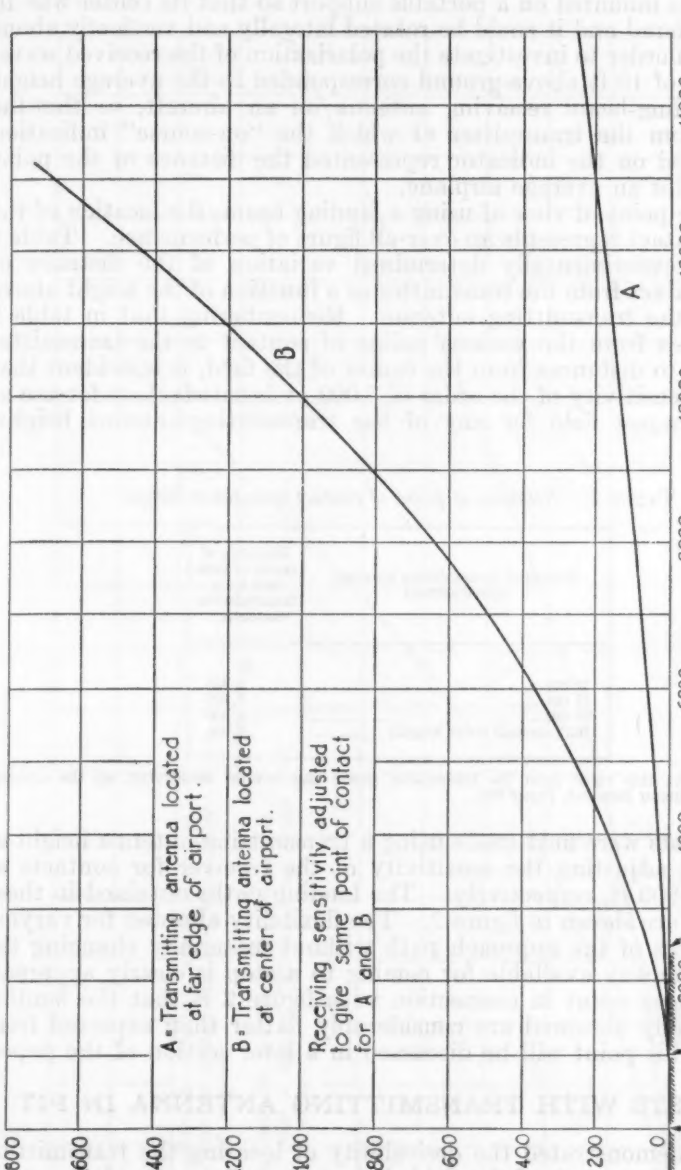

FIGURE 1.—*Approach paths corresponding to edge-of-field and center-of-field landing-beam locations.*

course") deflection of this indicator was approximately 5,000 μv. The antenna was mounted on a portable support so that its center was 10 ft above ground and it could be rotated laterally and vertically about its center in order to investigate the polarization of the received wave. The height of 10 ft above ground corresponded to the average height of the landing-beam receiving antenna on an aircraft, so that the distance from the transmitter at which the "on-course" indication was obtained on the indicator represented the distance of the point of contact for an average airplane.

From the point of view of using a landing beam, the location of the point of contact represents an over-all figure of performance. Table 1 shows the experimentally determined variation of the distance of point of contact from the transmitter as a function of the height above ground of the transmitting antenna. Remembering that in table 1 the distances from the various points of contact to the transmitter correspond to distances from the center of the field, it is evident that a receiver sensitivity of the order of 5,000 μv is satisfactory for use at even the largest field for any of the transmitting-antenna heights considered.

TABLE 1.—*Relation of point of contact to antenna height*

Height of transmitting antenna above ground	Distance of point of contact from transmitting antenna [1]
	ft
28 cm	1,300
51 cm	1,550
89 cm	1,800
165 (one-half wave length)	2,000

[1] For evaluating this value from the transmitter power and receiver sensitivity, see the equation on page 476 of Bureau Research Paper 602.

Flight tests were next made using a transmitting-antenna height of 30 cm and adjusting the sensitivity of the receiver for contacts at 1,300 and 800 ft, respectively. The landing paths obtained in these flight tests are shown in figure 2. The flexibility afforded for varying the steepness of the approach path without materially changing the length of runway available for coming to a stop is clearly apparent. An interesting point in connection with figure 2 is that the landing paths actually obtained are considerably flatter than expected from theory. This point will be discussed in a later section of the paper.

IV. TESTS WITH TRANSMITTING ANTENNA IN PIT

Having demonstrated the desirability of locating the transmitting antenna at the center of the field, it is necessary to consider some of the practical features incident to such location. The simplest arrangement is to place the transmitter in a pit and the antenna some 12 in. above the ground surface, feeding the antenna from the transmitter by a simple transmission line. Reasonable attention to preventing the accumulation of water or snow in the vicinity of the antenna would be sufficient to safeguard its electrical operation. However, the presence of such an antenna in the center of the airport presents some

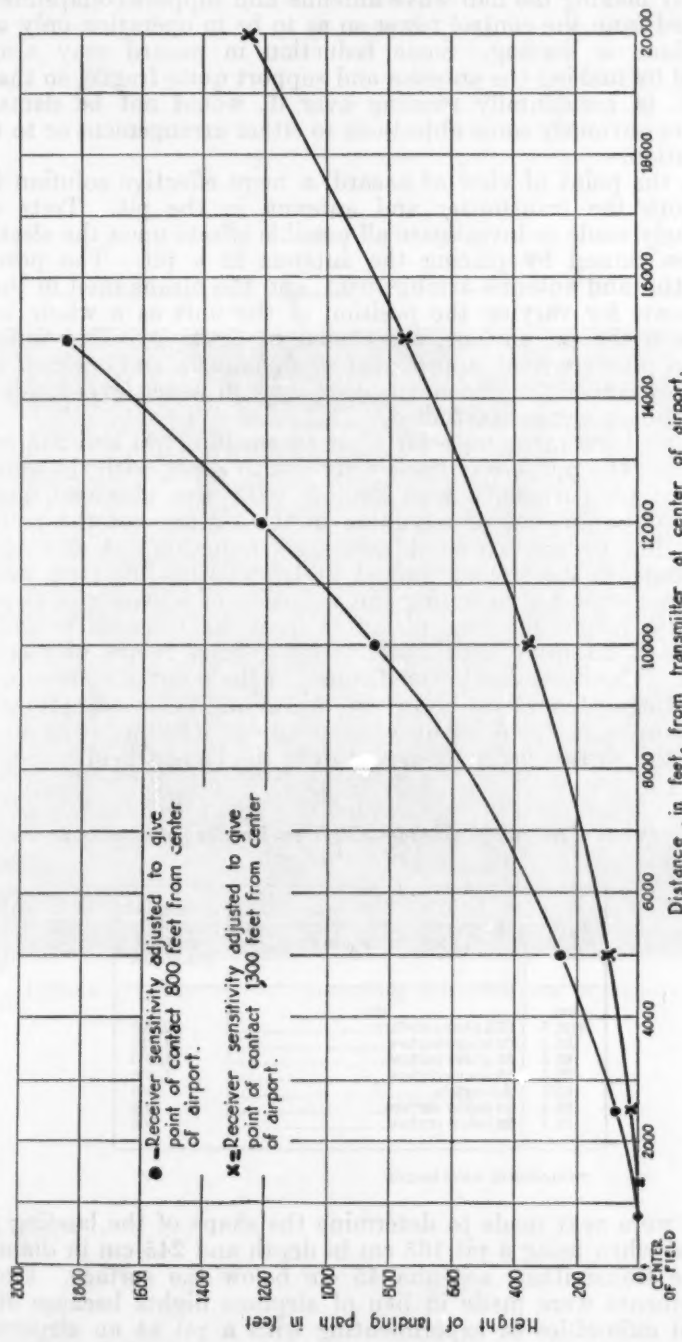

FIGURE 2.—*Typical approach paths possible with landing beam located at center of airport.*

hazard. It is likely that this hazard might be reduced to a negligible degree by making the half-wave antenna and support collapsible and controlled from the control tower so as to be in operation only while an airplane is landing. Some reduction in hazard may also be obtained by making the antenna and support quite fragile, so that an airplane, in accidentally running over it, would not be damaged. There are obviously some objections to either arrangement or to their combination.

From the point of view of hazard, a more effective solution is to place both the transmitter and antenna in the pit. Tests were accordingly made to investigate all possible effects upon the electrical operation caused by placing the antenna in a pit. The portable transmitter and antenna arrangement, and the means used in the pit experiments for varying the position of the unit as a whole below and above the pit surface, are shown in figure 3. Two different depths of pit were used, approximately one-fourth and one-half wave length, respectively. The effects of change in water level inside and outside the pit were also studied.

The first tests made were for a pit 80 cm in depth and 245 cm in diameter. The purpose of these tests was to see if, with the antenna below the pit surface, a true landing path was obtained, and to determine the amount of reduction in the distance of the point of contact due to the expected decreased radiation. A few simple experiments on the ground showed that a true landing path was set up. These consisted in noting the variation of intensity of received signal with height for fixed distances from the transmitter and the variation of intensity with distance for a fixed height of receiving antenna. The reduction in the distance of the point of contact as the transmitting antenna was brought down to and below the pit surface is shown in table 2. A receiver sensitivity of 5,000 μv is again seen to be of the correct order for use at even the largest field. (See figs. 1 and 2.)

TABLE 2.—*Points of contact resulting from different locations of antenna in relation to pit surface*

Depth of pit	Location of transmitting antenna relative to surface of pit	Distance of point of contact from transmitter
cm	cm	ft
[a] 82.5	82.5 above surface	2,000
82.5	60 above surface	1,750
82.5	30 above surface	1,200
82.5	15 above surface	1,100
82.5	At surface	950
82.5	10 below surface	900
82.5	20 below surface	900

[a] One-fourth wave length.

Tests were next made to determine the shape of the landing path produced when using a pit 165 cm in depth and 245 cm in diameter, with the transmitting antenna 45 cm below the surface. Ground measurements were made in lieu of airplane flights because of the practical difficulties of experimenting with a pit at an airport. A special receiving set was used with self-contained batteries and receiving antenna to permit hoisting up and down a pole. Figure 4

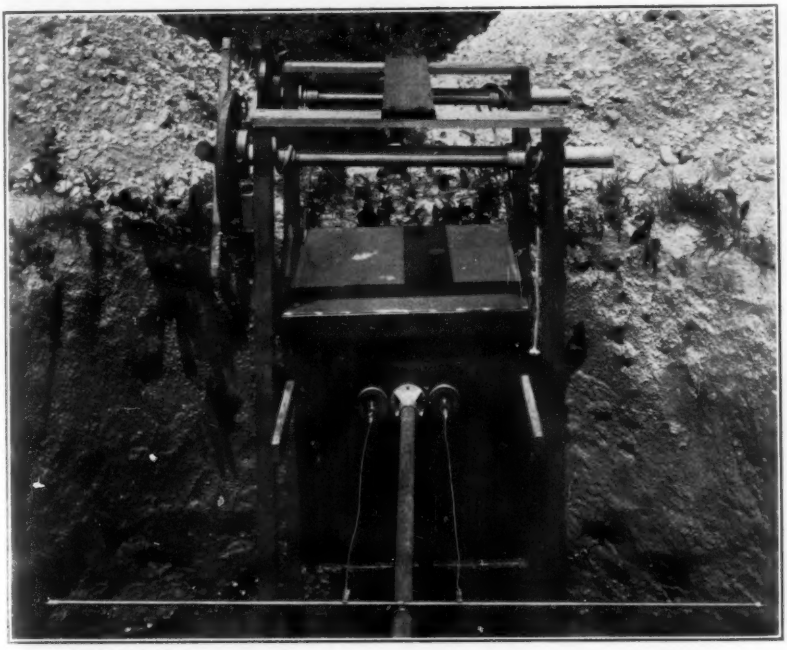

FIGURE 3.—*Experimental transmitting equipment used in the pit tests.*

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shows the variation of the intensity of received signal with height for two distances from the transmitter, 65 and 190 ft, respectively. The two graphs are plotted to adjusted ordinate scales so that they overlap, forming a single smooth curve. Figure 5 shows the variation of the intensity of received signal with distance from the transmitter at a fixed height for the receiving antenna. This latter graph was derived from data taken as follows. The receiver was adjusted for an arbitrary volume output at 50 ft from the transmitter and carried away from the transmitter until the signal intensity was halved. The volume output was then adjusted to its original value and the procedure

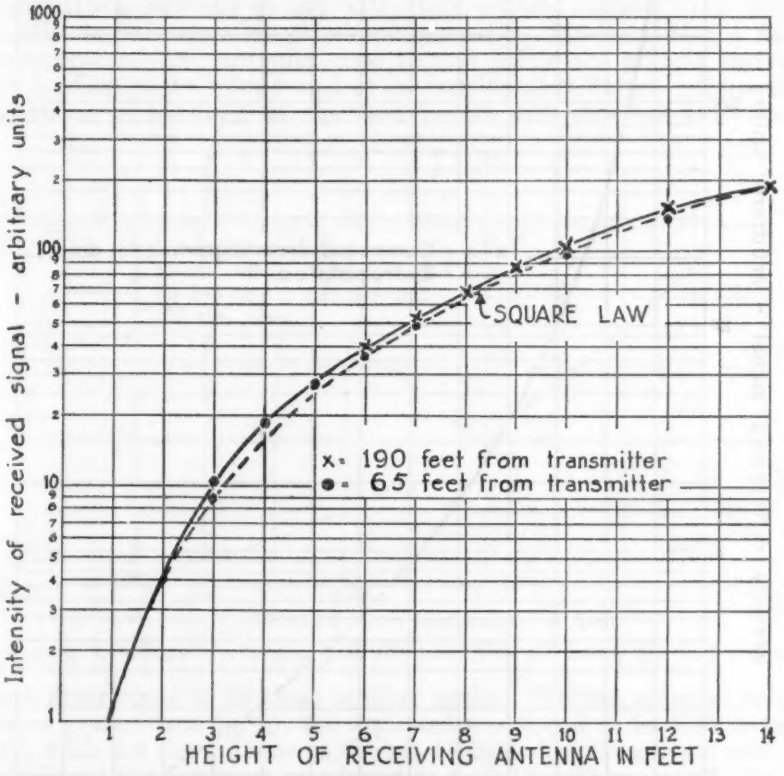
Intensity of received signal - arbitrary units
1000
100
10
1
SQUARE LAW
x = 190 feet from transmitter
● = 65 feet from transmitter
1 2 3 4 5 6 7 8 9 10 11 12 13 14
HEIGHT OF RECEIVING ANTENNA IN FEET

FIGURE 4.—*Vertical distribution of intensity of received signal in field radiated from transmitting antenna in pit.*

repeated again and again, the distance from the transmitter being recorded corresponding to each adjustment of volume. A value of 8 was arbitrarily chosen for the signal intensity at the farthest point measured, 310 ft.

From figures 4 and 5 it is possible to compute the landing path corresponding to a given signal intensity. Thus assume that at 50 ft from the transmitter, the output volume indicator deflects to one-half scale at a height of 1 ft. At 100 ft from the transmitter, the received signal at 1-ft height is one-tenth of that at 50-ft distance (see fig. 5). To return to the original received signal, it is necessary to raise the receiving antenna to 3.2 ft (see fig. 4). This is a second point on the

landing path. The complete landing path, derived in this way, is shown in figure 6. There is of course a family of such paths, the steepness depending entirely on the intensity of the line considered. Corresponding to a height of 10 ft at distances of 800 and 1,300 ft from the transmitter, the landing paths would be somewhat flatter than

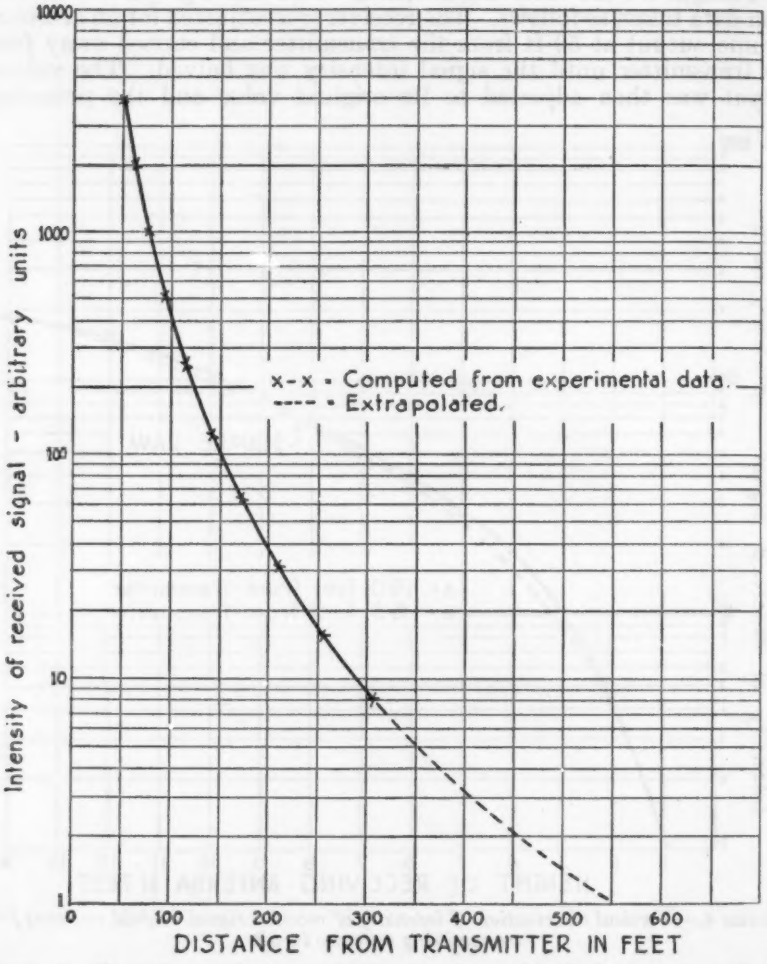

FIGURE 5.—*Variation of the intensity of received signal with distance from the pit transmitting antenna, corresponding to a constant height of the receiving antenna.*

those shown in figure 2 (for the transmitting antenna 30 cm above ground).

V. STUDY OF SHAPE OF LANDING PATHS

It is of interest to note the effect of the proximity of the ground to the transmitting antenna upon the shape of the lines of constant received signal forming the landing paths. As will be shown later in

this section, the theoretical equation of the landing path may be stated as

$$y=y_0(r/r_0)^2, \tag{1}$$

where

y_0 = the height of the receiving antenna above the bottom of the landing gear,
r_0 = the distance of the point of contact from the transmitter,
r = distance from the transmitter,
y = corresponding height of the landing path.

Experimentally, this equation was checked closely when using directive transmitting antenna arrays with their centers located from three-fourths to one wave length above ground.[2] However, with a half-wave transmitting antenna close to and below the ground surface, the landing paths were found to be considerably flatter. Empirical equations of the form of equation 1, but with different exponents,

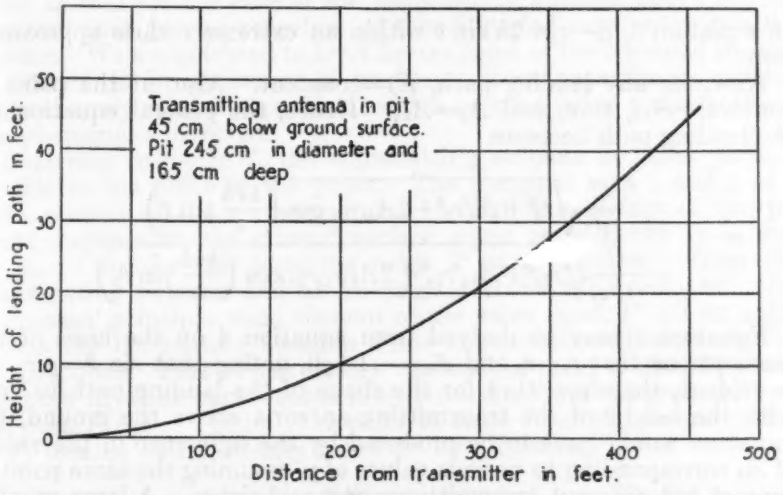

FIGURE 6.—*Shape of a landing path computed from the data of figures 4 and 5.*

were determined to fit these landing paths. For the antenna 30 cm above ground (see fig. 2), the exponent was found to be 1.85 instead of 2, while for the antenna in the pit 45 cm below the ground surface (see fig. 6) the exponent was found to be 1.75. There would appear to be a steady transition in the shape of the path as the antenna is brought down to and below the ground surface. As a check on the trend of this transition, a further test was made with the transmitting antenna 15 cm above the ground surface. For this case, the shape of the path was found to be very nearly the same as for the antenna in the pit. The difference in the shape of the paths under the different test conditions is possibly caused by the fact that when the antenna is near the ground, the wave incident on the ground is no longer plane, so that equation 1, which is based on the assumption of plane-wave ground reflection, does not hold.

The derivation of equation 1, showing that other assumptions involved do not contribute to the apparent departure from the plane-

[2] See footnote 1, p. 1.

wave theory, follows: Given an antenna h units above the ground and its image at similar distance below the ground. For unit antenna current, the electric field set up at a point P (at a height y above ground, at a distance r from the point on the ground surface just below the antenna, and making an angle θ with the ground) is

$$E_P=C\left\{\frac{1}{r_2}\cos\omega\left(t-\frac{r_2}{V}\right)+\frac{A_h}{r_1}\cos\omega\left(t-\frac{r_1}{V}\right)\right\}, \tag{2}$$

where A_h is the complex reflection coefficient for horizontally polarized waves, and r_2 and r_1 are the distances between the point P and the antenna and its image, respectively. The amplitude of E_P may be written as equation 3, remembering that $\omega/V=2\pi/\lambda$

$$E_P=\frac{C}{r_1r_2}\sqrt{r_1^2+A_h^2r_2^2+2A_hr_1r_2\cos\frac{2\pi}{\lambda}(r_1-r_2)} \tag{3}$$

In equation 3, $r_1-r_2=2h\sin\theta$ within an extremely close approximation.

Now, for any landing path, E_P=constant. Also, at the point of contact, $r=r_0$, $\theta=\theta_0$ and $A_h=A_{h_0}$. Hence, the general equation for the landing path becomes

$$\frac{C}{r_1r_2}\sqrt{r_1^2+A_h^2r_2^2+2A_hr_1r_2\cos\left(\frac{4\pi h}{\lambda}\sin\theta\right)}$$
$$=\frac{C}{r_{1_0}r_{2_0}}\sqrt{r_{1_0}^2+A_{h_0}^2r_{2_0}^2+2A_{h_0}r_{1_0}r_{2_0}\cos\left(\frac{4\pi h}{\lambda}\sin\theta_0\right)} \tag{4}$$

Equation 1 may be derived from equation 4 on the basis of the assumptions that $r_1=r_2$ and $A_h=-1+j0$, noting that $\sin\theta=y/r$. It is evident, therefore, that for the shape of the landing path to vary with the height of the transmitting antenna above the ground, the variation would have to be produced by the difference in the values of A_h corresponding to various values of y, assuming the same point of contact but different transmitting-antenna heights. A large number of computations, corresponding to possible practical values of h, y_0, r_0, and the electrical ground constants, showed that this is not the case. It would, therefore, appear that the variation must be caused by the lack of planeness of the radiated wave.

VI. THEORY UNDERLYING OPERATION OF LANDING-BEAM ANTENNA IN PIT

The fact that a landing path is set up with the transmitting antenna located inside the pit presents a study in the optical behavior of the ultra-high-frequency radiations. In an attempt to arrive at a theoretical analysis of the phenomena involved, two approaches present themselves. The first is that the rays penetrate the sides of the pit and emerge at the earth's surface. The vertical distribution of energy obtained may then be assigned to the fact that rays at the lower angles have the longer optical paths and hence the greater attenuation. There is quite strong evidence, however, that this is not the actual case. Firstly, an experiment was made in which the walls of the pit were lined with a copper shield. This resulted in negligible change in

attenuation of the transmitted wave. At a distance of 190 ft. from the transmitter, the intensity of the received signal and its variation with height were very nearly the same with and without the shield. Furthermore, an examination of the angles involved shows that even were the rays transmitted through the walls of the pit, they would reach the ground surface at such angles as to require total internal reflection; there could thus be no rays emerging at the ground surface.

The next likely explanation of the phenomena involved is that the rays are diffracted around the rim of the pit, the intensity of radiation dropping off as a function of the angular deviation below the marginal rays just clearing the rim. The experimental evidence pointed to this theory as a plausible one. A marked change in the water content in the surrounding ground and also shielding the walls of the pit, introduced no appreciable change in either the intensity of received signal or its vertical distribution. However, the fact that the shape of a line of constant received signal was so very nearly the same as that for the case of the transmitting antenna above ground required that ground reflection of the diffracted rays enter into the picture. We are indebted to Dr. Chester Snow of the National Bureau of Standards for assistance in working out an approximate mathematical analysis of this problem, which serves to give a clear idea of the phenomena involved.

Referring to figure 7, the transmitting antenna is taken perpendicular to the plane of the paper. The marginal rays 1 and 2 of a right section of the wave emerging through the surface of the pit make angles with the ground surface equal respectively to ϕ_0 and $\pi-\phi_0$. Consider the receiving point P at a distance r from the transmitting antenna and at an angle θ above the horizontal. By Huyghens' principle, each element of the wave front, P' (at an angle ϕ with the horizontal), becomes a new source and radiates energy in all directions. Part of this energy reaches the point P directly along the path R, while part reaches it by reflection from the ground along the path $P'P_3P$. The latter appears to come from the virtual image of P' located at P_1, directly below P' by a distance,

$$2h=2a(\sin\phi-\sin\phi_0) \tag{5}$$

It is possible to assume an image under the general point P', even though the surface of the reflecting plane is cut away from below it, since, for the angles of θ involved, the actual reflecting point P_3 always falls beyond the rim of the pit. The intensity at P due to the two rays from P' may then be set up in terms of the various distances and angles indicated on figure 7, and it may be summed for all the elementary points on the wave front between the limits of the marginal rays, as indicated in the expression

$$E_r=\frac{A}{r}\int^{-\phi_0}\left\{1+\cos\phi\right\}\left\{\sin\omega\left[t-\frac{a+R}{V}\right]-\sin\omega\left[t-\frac{a+R'}{V}\right]\right\}d\phi, \tag{6}$$

where $(1+\cos\phi)$ is the Stokes' obliquity factor taking into account that the new wavelet at P' tends to be propagated with maximum effect in the direction of propagation of the original wave front at this point. Equation 6 involves the assumption that $\alpha=\phi$, since θ, being always less than 3 degrees, is small compared to ϕ. In

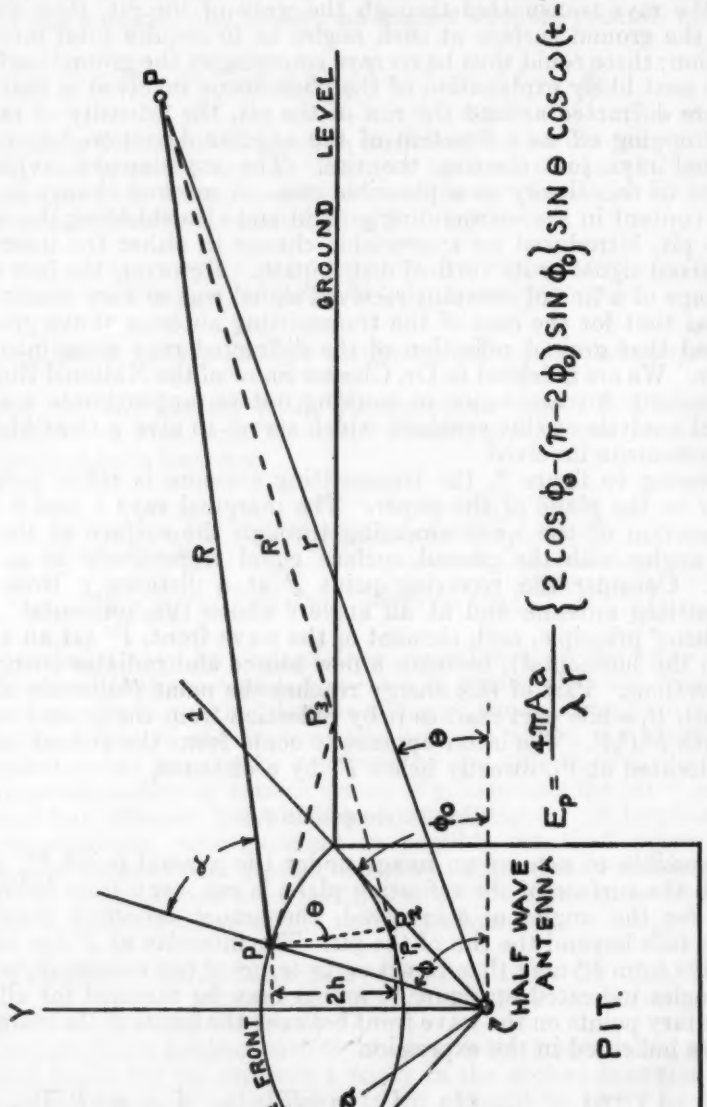

FIGURE 7.—*Mechanism of setting up a landing path with the transmitting antenna in a pit.*

equation (6,) $a+R/V$ is the phase retardation with respect to the phase at the antenna of the wave reaching P along the path R, and $a+R'/V$ is the phase retardation of the wave reaching P via $P'P_3P=R'$. The negative sign is taken before this term to indicate a negative image. Placing

$$R=r-\frac{R'-R}{2} \text{ and}$$

$$R'=r+\frac{R'-R}{2}$$

we may write from equation 5 and from the fact that $R'=R+P_1P_2=R+2h \sin\theta$ approximately

$$\left.\begin{aligned} R&=r-a.\sin\theta(\sin\phi-\sin\phi_0)\\ R'&=r+a.\sin\theta(\sin\phi-\sin\phi_0)\end{aligned}\right\} \tag{7}$$

substituting equation 7 in equation 6, we have

$$E_p=\frac{A}{r}\int_{\phi_0}^{\pi-\phi_0}\left\{1+\cos\phi\right\}\left\{\sin\omega\left(t-\frac{a+r}{V}+\frac{a\sin\theta(\sin\phi-\sin\phi_0)}{V}\right)\right.$$

$$\left.-\sin\omega\left(t-\frac{a+r}{V}-\frac{a\sin\theta(\sin\phi-\sin\phi_0)}{V}\right)\right\}d\phi \tag{8}$$

Simplifying

$$E_p=\frac{2A}{r}\cdot\cos\omega\left(t-\frac{a+r}{V}\right)\int_{\phi_0}^{\pi-\phi_0}\left\{1+\cos.\phi\right\}\left\{\sin\left[\frac{\omega a}{V}\sin\theta\,(\sin\phi\right.\right.$$

$$\left.\left.-\sin\phi_0)\right]\right\}d\phi \tag{9}$$

But since θ is small, $\sin\left[\frac{\omega a}{V}\sin\theta(\sin\theta-\sin\phi_0)\right]=\frac{\omega a}{V}\sin\theta\left(\sin\phi-\sin\phi_0\right)$

Also $\omega a/V=2\pi a/\lambda$

Therefore

$$E_p=\frac{4\pi Aa}{\lambda r}\cdot\cos\omega\left(t-\frac{a+r}{V}\right)\cdot\sin\theta\cdot$$

$$\int_{\phi_0}^{\pi-\phi_0}(1+\cos\phi)\,(\sin\phi-\sin\phi_0)d\phi \tag{10}$$

Integrating

$$E_p=\frac{4\pi Aa}{\lambda r}\cdot\left\{2\cos\phi_0-(\pi-2\phi_0)\sin\phi_0\cdot\right.$$

$$\left.\sin\theta\cos\omega\left(t-\frac{a+r}{V}\right)\right. \tag{11}$$

Equation 11 gives the field intensity at the point P in terms of the angle of elevation θ, the dimensions of the pit, and the wave length in air. For a pit of given dimensions and with the antenna in a given position, equation 11 resolves into

$$E_p = C \sin\theta \cos 2\pi f\left(t - \frac{a+r}{V}\right) \tag{12}$$

The latter equation indicates that the intensity at the point P is a sine function of the angle of elevation of the point P. Since for small angles, $\sin\theta = \theta$, the vertical distribution of intensity is seen to be a linear function of the height. In our experiments, we obtained a square law function. (See the dotted curve in fig. 4.) However, the receiver used was of the triple-detection type of which the law of relation between output and input was probably close to a square law, so that there is fair agreement between the theory and the experimental data.

Referring to equation 11, the first group of factors indicates that for a given antenna location in the pit, the intensity P increases with the opening of the pit (i. e., with its diameter) and decreases with an increase in the wave length used. The portion of equation 11 in braces shows that for a given pit diameter, the intensity at P is a function of the angle of the marginal ray; i. e., of the depth of the antenna in the pit. A study of this term discloses that the intensity is large for small angles of ϕ_0 and decreases as ϕ_0 is increased, becoming zero for $\phi_0 = \pi/2$. The factor $\sin\theta$ in equation 11 gives the relation of the intensity with the angle of elevation of the receiving point, while the remaining cosine function indicates the phase of the resultant field at the receiving point.

From the foregoing analysis, it becomes apparent why the path of a line of constant field intensity is of very nearly the same shape with the transmitting antenna in the pit as for the antenna a short distance above the ground surface. The wave front emerging from the pit is practically equivalent to a physical antenna above the ground surface, so that the phenomena of interference between a direct and reflected wave may occur. From the trend of change of path shape with proximity of the antenna to the ground (discussed in section V), the equivalent height of the experimental combination used to set up the landing path of figure 6 was approximately 15 cm.

VII. POLARIZATION OF THE RECEIVED WAVE

A study of the polarization of the electric field corresponding to different positions of the transmitting antenna above the ground surface and above and below the pit surface revealed further evidence of the effect of the ground proximity. It was found that the ratio of vertically to horizontally polarized electric-field component radiated from the horizontal antenna at various azimuth angles on either side of the normal to the length of the antenna was much greater than expected as the antenna was brought close to the ground surface. For the receiving antenna at a distance of 100 m and at a height of 3 m the ordinary theory requires that the ratio be very small because of the very small angles of elevation involved.

Figure 8 shows the data obtained for the transmitting antenna at various heights above the ground surface. Each set of curves on

this figure corresponds to a fixed position of the transmitting antenna and shows the relative amplitudes of the horizontally and vertically polarized electric field components as a function of angle (in the horizontal plane) on either side of the normal to the transmitting antenna. The magnitude of the vertically polarized electric field and the rapid increase in the ratio of vertical to horizontal field component as the transmitting antenna is brought closer to the ground are far beyond what would be expected from the plane-wave theory.

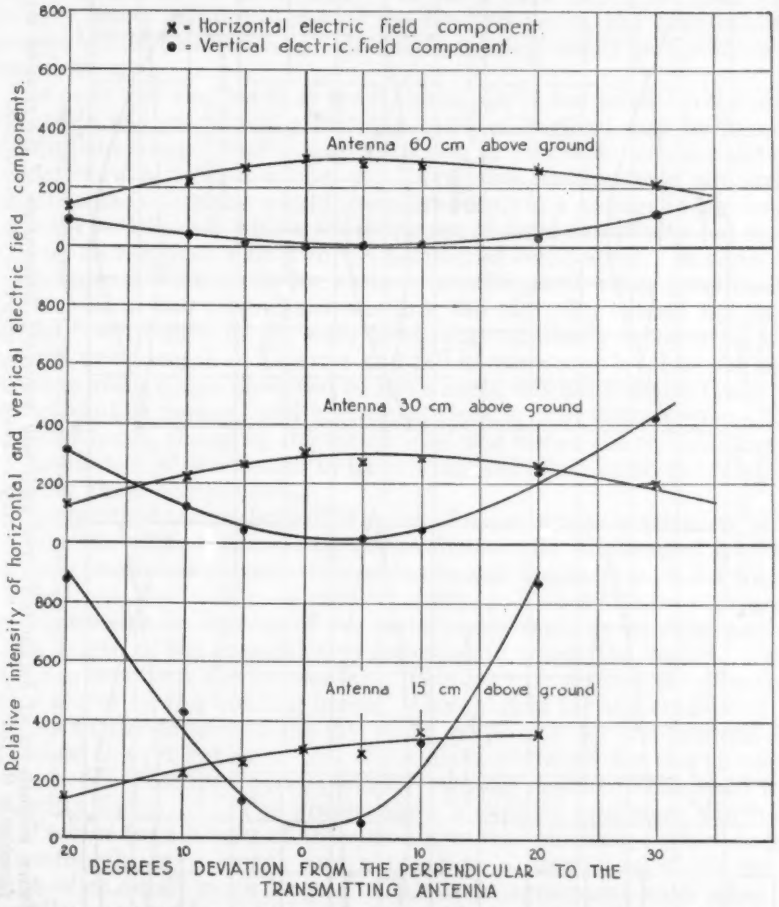

FIGURE 8. *Relative magnitudes of horizontally and vertically polarized components of the received wave as a function of height of transmitting antenna above the ground surface.*

Figure 9 shows similar data for the transmitting antenna at various positions with respect to the surface of a pit approximately one-fourth wave length in depth (80 cm). A study of figure 9 in comparison with figure 8 brings out the following points:

1. For equivalent heights above the pit surface and above actual ground surface, the relative amount of vertically polarized component is considerably lower for the former.

2. The relative amount of vertically polarized component for departures from the normal of $\pm 15°$ is negligible until the antenna approaches within 60 cm of either the pit or the ground surface.

3. In the case of the experiments with the pit having a depth of one-fourth wave length, the relative amount of vertical component

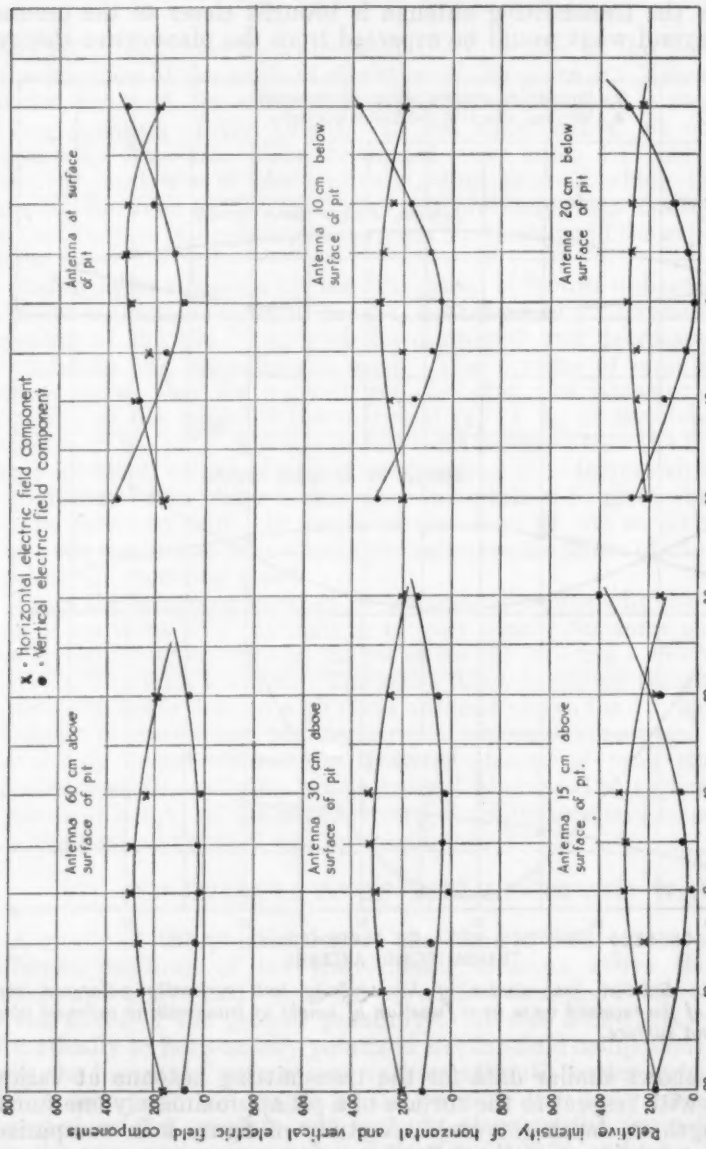
× - Horizontal electric field component
● - Vertical electric field component
Antenna 60 cm above surface of pit
Antenna at surface of pit
Antenna 30 cm above surface of pit
Antenna 10 cm below surface of pit
Antenna 15 cm above surface of pit.
Antenna 20 cm below surface of pit
Relative intensity of horizontal and vertical electric field components
DEGREES AZIMUTH DEVIATION FROM THE PERPENDICULAR TO THE TRANSMITTING ANTENNA

FIGURE 9. *Relative magnitudes of horizontally and vertically polarized components of the received wave as a function of the position of the transmitting antenna with respect to the pit surface.*

increases as the antenna approaches from 60 cm above the surface to the surface and then would appear to decrease gradually as the antenna is brought to 20 cm below the surface.

There was a twofold reason for our interest in the presence of an appreciable vertical component in the radiated field. Firstly, such

a component results in a tilt of the plane of polarization of the total electric field, so that tilting of the airplane receiving antenna on either side of its normal horizontal position would result in different readings of the landing path "course" indicator. Secondly, since the vertical component is not useful it represents an actual waste of energy. The first reason does not become important until the ratio of vertical to horizontal component becomes greater than unity for angular departures of less than $\pm 10°$ from the normal direction to the transmitting antenna. A little study will show that this is the case particularly since, in normal use of the landing beam, the transmitting antenna would be oriented at all times perpendicularly to the existing wind direction.

The next test was made to see if the depth of the water level inside or outside the pit would affect the ratio of vertical and horizontal electric-field components. Any variation in this ratio would indicate a transfer of a portion of the total available energy from one component to the other and would therefore result in a change in the landing path, as followed with a receiving set of fixed sensitivity fed from an antenna responsive only to the horizontal component. A series of measurements were made for various conditions of water level inside the pit and in the ground surrounding the pit. To extend the data secured, two depths of pit were used, approximately one-fourth and one-half wave length. The rise and fall of the water level in the surrounding ground was observed to have negligible effect upon the relative amount of vertical and horizontal electric field components. On the other hand, changing the water level and hence the reflecting surface inside the pit was found to have a marked effect upon the relative values of these components.

The results obtained from this series of measurements are correlated in figure 10. The abscissas represent distance in fractions of a wave length between the transmitting antenna and the surface of the water in the pit (or the bottom of the pit, if dry). The ordinates represent the total width in degrees of the sector, substantially at right angles to the length of the transmitting antenna, in which the vertical component is less than the horizontal. This may be termed the effective useful sector of the landing beam. Graph *A* is for the transmitting antenna at the surface of the pit, while graph *B* is for the antenna 20 cm below the pit surface. All of the data obtained for the antenna in these two positions corresponding to both depths of pit used are plotted in figure 10. The graphs show a definite minimum width of useful sector for a height of antenna above the reflecting surface equal to one-fourth wave length and a trend to a maximum width for a height of one-half wave length. This is in agreement with what is normally expected for the case of a transmitting antenna above ground.

Unlike the case for a transmitting antenna above ground, the relative amount of vertical component in the radiated field is very much greater. This is probably attributable to the effect of the proximity of the ground to the high-voltage ends of the transmitting antenna, which may result in the production of a vertical current. There is some experimental basis for believing this to be the case. In some of the tests made, it was observed that varying the position of the antenna below the pit surface and at the same time keeping the effective reflecting surface at a constant distance below the antenna did not result in the same relative amount of vertical component.

The difference in the net proximity effect of the sides of the pit for the various antenna positions may be offered as an explanation of this phenomenon. This effect is indicated by the graphs of figure 10, graph *A* for the antenna at the pit surface showing, on the average, a greater width of useful sector than graph *B*, which corresponds to the antenna at 20 cm below the pit surface.

From the practical point of view, insofar as use of the landing beam transmitting antenna in a pit is concerned, it is possible to provide for an unchanging ratio of the two components by waterproofing the pit. This will result in an unvarying amount of energy in the horizontal electric field (for a given transmitter power) and hence in a fixed landing path.

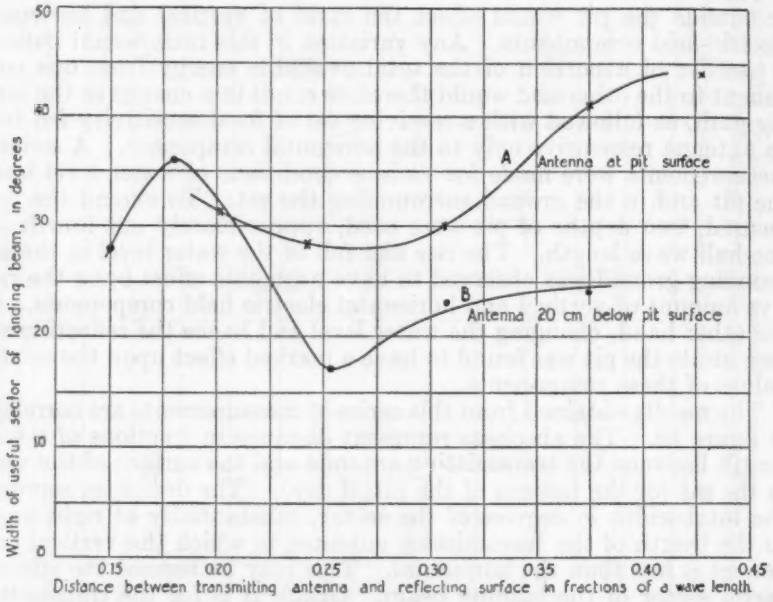

FIGURE 10. *Effect of distance between transmitting antenna and reflecting surface at bottom of pit upon relative magnitudes of horizontal-and vertical-field components.*

Ordinates denote the width of sector, normal to the transmitting antenna, wherein the horizontal component is greater than the vertical.

VIII. CONCLUSIONS

As a result of the various experiments outlined, the following conclusions may be drawn.

A very material increase in the flexibility of use of the landing beam, particularly in providing a suitably steep approach path to large airports, may be obtained through employing a half-wave transmitting antenna located at the center of the airport. The antenna may be a small fraction of a wave length above the ground surface or in a pit below the ground surface. In either case the proximity of the ground to the horizontal transmitting antenna introduces interesting effects upon the electric field radiated.

As the transmitting antenna is brought closer to the ground surface, the shape of a line of constant field intensity in the radiated

field (for angles of elevation less than 3 degrees) departs from a parabola, becoming somewhat flatter. The effect appears to be the same for the antenna in a pit as when it is just above the ground surface. This arises from the phenomena involved in the radiation of an electric field from the transmitting antenna located in the pit. The wave front emerging from the pit operates as a large number of new sources which produce direct radiation to the receiving point and also indirect radiation by way of reflection from the ground surface. The two sets of radiation produce an interference pattern very similar to that produced by a transmitting antenna a short distance above ground.

The proximity of the ground to the transmitting antenna also increases the relative amount of vertically polarized electric field in the emitted wave. This effect may be limited through use of the pit. The depth of the pit should be of the order of one-half wave length, corresponding to which the width of useful sector of the landing beam is a maximum. The pit should be waterproofed so that water cannot enter it from the surrounding ground, and thereby change its effective depth. The proximity effect may be further limited by keeping the walls of the pit away from the ends of the transmitting antenna; the minimum cross-sectional dimension should be at least three-fourths of a wave length.

The walls and bottom of the pit may be lined with shielding material in order to render constant the radiation losses to the surrounding ground. The roof of the pit, required for the protection of landing airplanes, must be of a nonconducting material of low dielectric constant to permit of free emergence of the radiated wave.

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SOME PROPERTIES AND TESTS OF TRAFFIC OR ZONE PAINTS [1]

By Eugene F. Hickson

ABSTRACT

This publication describes some properties and tests of traffic paints. These paints are of a different type from ordinary paints and vary greatly in abrasion resistance. Experience gained from actual road tests is cited. An accelerated wearing test is described. A distinct improvement in durability of the traffic paints in actual service has resulted. Specifications for white and yellow traffic paints are suggested.

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I. INTRODUCTION

Traffic or zone paints are used to an increasing extent for marking off street-car loading areas, cross walks, "islands" of safety for pedestrians, center line stripes on city and State roads, caution and other warning signs on roads, etc. Materials other than paint, such as metal "buttons", inserts of white brick, white plastics, white cement, mixtures of black asphalt emulsions and sand, and strips of painted cloth, all used for the same purpose as traffic paint, are not considered in this publication.

The only publications of any length, with which the writer is familiar, describing experimental work on traffic paint, are those of Nelson and Werthan, and Sweatt.[2]

While the present publication deals mainly with white traffic paint, it should be noted that colors such as bright red, yellow, orange, and black are used in some States. Whatever the color, the paint must be suitable for any kind of hard pavement, have good consistency, flow evenly and smoothly, dry rapidly, hide in one coat, be of a brilliant color, show good color retention, dry hard and tough, be resistant to water, oil, and grease, show good day and night visibility, and be extremely durable (resistant to both weather and abrasion). Some paint manufacturers make one type of paint for concrete roads, and

[1] This paper is also printed as Circular 532, Scientific Section, Ntl. Paint, Varnish, and Lacquer Assn., Inc., Wash., D. C.

[2] H. A. Nelson and S. Werthan, Ind. Eng. Chem. 18, 965 (1926). John H. Sweatt, Paper 19, Maine Technology Experiment Station, University of Maine, Orono, Maine.

another for bituminous roads. Some make paint designed separately for use in summer and winter, so that at all times the paint will be rapid-drying.

Because large quantities are used, the cost of traffic paint is an important consideration. There are three elements which enter into the ultimate cost: The cost of the paint itself, the cost of application, and the durability. The cost of application is at least twice the cost of the paint itself, and may be in even greater proportion. Durability may vary as much as 2 to 1. If paint *A* costs $1 a gallon and wears for 3 months, where paint *B* costs $1.50 per gallon and wears for 5 months, and the cost of application is $3 a gallon in each case, the ultimate cost of paint *A* is about 4½ cents per gallon-day, while paint *B* really costs 3 cents per gallon-day of use.

II. CHARACTERISTICS OF THE PAINT

Generally, traffic paints are fairly heavily pigmented, so that they dry to flat or semigloss finishes—rarely to gloss finishes. Frequently, they are made purposely of a thick consistency, so that they can be thinned on the job, generally with gasoline. However, traffic paint should not be thinned excessively with gasoline, or its durability will suffer. A heavy-bodied traffic paint, provided it can be brushed or applied by machine, is apt to wear longer than a thin-bodied paint, because a thicker film is formed, assuming other properties equal. In white paint, the opaque pigments are selected for suitable color and efficient hiding power at minimum cost. The pigments generally used are lithopone, zinc oxide, and titanium-base pigments. A certain amount of silicate-base pigments, such as china clay, magnesium silicate, silica, sand, pumice, etc., are added to increase resistance to wear, the last two mentioned materials being added also to increase visibility at night by imparting roughness to the film. Extremely small glass spheres distributed on the wet paint coat are also used for the same purpose. In paints other than white, pigments such as carbon black, iron oxide, and organic reds, chrome yellows and chrome oranges are used. Large amounts of the silicate-base pigments are added to these colors as diluents. Some zinc oxide is also beneficial for color retention in the yellow and orange colors.

Whatever the color, the vehicles or liquid portions of traffic paints of a single brand are usually the same. Generally, the vehicle is a quick-drying varnish. In the better grades, china-wood oil–rosin varnishes containing from 10 to 40 gallons of oil per 100 pounds of rosin may be employed. Ester gum and gum copals may be added to improve the adhesive properties of the film. Besides the resins, oils, and driers, traffic paints contain a large amount of volatile thinners, selected to promote the rapid drying of the paint film. The thinners are usually low-boiling fractions from petroleum or coal tar, including gasoline or varnish-makers' and painters' (V. M. & P.) naphtha and benzol. In some paints, the vehicle is a cold-cut resin, such as East India gum (powdered Batu or Macassar), or manila or damar resin dissolved in mineral spirits or, sometimes in such solvents as alcohol (formula 1), acetone, or butyl alcohol. Occasionally, blown linseed, tung, or other oil is added as a plasticizer.

Rubber latex and clear cellulose lacquers are also employed as vehicles; and water-vehicle paints, such as those made from casein, glue, and sodium silicate are sometimes used.

III. ROAD EXPOSURE TESTS

About 10 years ago, the National Bureau of Standards began testing traffic paints for and in cooperation with officials of the District of Columbia. Since that time the working properties of many paints in a road distributing machine and the "mileage", how long a stripe 4 inches wide can be made with 1 gallon of paint, have been determined by the District officials, while such physical tests as hiding power, reflectance, consistency, drying time, tendency of the bitumen to "bleed" (stain the paint above), and relative durability in actual service on the road have been determined at the Bureau.

The tests last mentioned were made on Connecticut Avenue, near the Bureau. Parallel stripes of the various paints, about 4 inches wide and about 15 feet long, spaced about 1 foot apart, were applied, mostly by hand brushing. The stripes were made on the road on one side of the avenue (south-bound traffic) from the curb to the car tracks in the center. Fortunately, one portion of the road was concrete, while the rest was bituminous material, so that the same paints were applied at the same time on both types of surfaces. On both portions of the road there was a gradual change in the number of automobiles to which the paint was exposed, varying from a maximum near the middle of the roadway to minima at the curb and at the car track. Traffic on the avenue was fairly heavy, but not as heavy as in congested traffic areas. A traffic count showed that, on a particular day, 4,600 cars passed over the test area in 7 hours from 8 a. m. to noon and from 3 to 6 p. m. The area lies in a 22-mile speed zone.

A great variety of paints were applied to the road, including both commercial brands and experimental paints. Among the types of experimental paints studied were the following:

1. Paints with a vehicle made from wood oil and ester gum in various proportions from 10 to 20 gallons of oil per 100 pounds of gum. With this vehicle the following pigments were used: (a) 90 percent of lithopone, 10 percent of magnesium silicate; (b) 65 percent of lithopone 25 percent of zinc oxide, 10 percent of magnesium silicate; (c) 90 percent of titanium-barium pigment, 10 percent of magnesium silicate; (d) 65 percent of titanium-barium pigment, 25 percent of zinc oxide, 10 percent of magnesium silicate.

2. Paints with a vehicle made from wood oil and modified phenolic resin in various proportions from 10 to 20 gallons of oil per 100 pounds of resin. The same series of pigments were used as with the paints of the first type.

3. Cold-cut East India gum (Batu) plasticized with a small amount of blown linseed oil, with a pigment containing 55 percent of titanium pigment, 25 percent of zinc oxide, and 20 percent of silica.

4. Spar varnish with aluminum powder (2 lb of powder to 1 gallon of varnish).

5. Straight-gloss oil vehicle (limed rosin dissolved in mineral spirits), with a pigment containing 65 percent of lithopone and 35 percent of silica.

6. A paint made with a solution of sodium silicate in water (a commercial brand known as Paint Vehicle) and a pigment consisting of 70 percent of lithopone, 20 percent of zinc oxide, 10 percent of silica. Also the same paint with the addition of rubber latex (50 ml of rubber latex added to 1 pint of paint).

7. Hydrated-lime–casein–cold-water paint consisting of 100 parts of hydrated lime, 20 parts of casein, 12 parts of trisodium phosphate, and 30 parts of whiting.

8. Rubber paints with lithopone and magnesium silicate and with aluminum powder pigments. The vehicle was a commercial product consisting of a rubber isomer in an organic solvent.

In general, the paints did not wear as well on concrete as on bitumen. However, some paints wore better on concrete. Some were satisfactory on concrete, but caused the bitumen to "bleed", changing the white color of the paint to a brownish or yellowish white. The usual life of the best paints was about 3 months. Some of the paints were worn off in less than 3 weeks. The paint near the car tracks and near the curb lasted several times as long as that in the center of the roadway, showing that weathering was of minor importance as compared with wear under the conditions of testing.

In repeated trials, one brand of paint was consistently the best of the commercial paints. This paint was, therefore, used as a "control" in comparing the durability of more recent brands and of all experimental paints. Chemical analysis failed to reveal the reason why this paint was so durable. The vehicle appeared to be a tung-oil–rosin varnish. The pigment was a mixture of 30 percent of lithopone, 40 percent of zinc oxide, and 30 percent of siliceous matter. The separated vehicle dried to a hard, very tough, and adherent film, and contained 45 percent of nonvolatile matter.

Two of the best experimental paints were of the following compositions, expressed in percentages by weight unless otherwise indicated:

Paint 1 contained 65 percent of pigment and 35 percent of vehicle. The pigment was 65 percent of light-proof lithopone, 25 percent of lead-free zinc oxide, and 10 percent of magnesium silicate.

The vehicle was a varnish made in the proportions of 9 gallons of china wood oil and 6 gallons of linseed oil per 100 pounds of modified phenolic resin and thinned with V. M. & P. naphtha and drier to contain 40 percent of nonvolatile material.

Paint 2 contained 65 percent of pigment and 35 percent of vehicle. The pigment was 56 percent of titanium-barium pigment, 24 percent of lead-free zinc oxide, 10 percent of magnesium silicate, and 10 percent of silica. The vehicle was again 40 percent nonvolatile and made of the same constituents as the first, but in the proportions of 12 gallons of china wood oil and 8 gallons of linseed oil per 100 pounds of resin.

The results of the road tests quickly demonstrated that the character of the vehicle is far more important than that of the pigment in a traffic paint. However, the addition of zinc oxide to either lithopone or titanium pigment improved durability. The presence of some abrasion-resisting inert of the siliceous-base type is also desirable.

It was also observed that several commercial paints, all passing the same specification based on composition, gave different results during wear tests. It is not possible to state whether or not these paints were of identical composition. Methods of analysis of the vehicle of a paint are not exact enough to identify and determine the amounts of resin and oil present. Even if this were possible, chemical analysis would not reveal how the resin and oil were processed in the varnish kettle. This processing procedure affects the properties of the vehicle.

Thus, a consumer's specification for traffic paint should be based on physical and performance tests, rather than on a formula which purports to describe the composition.

IV. MACHINE FOR ACCELERATED WEARING TEST [3]

In order to test resistance to abrasion more quickly under more accurately controlled conditions, an accelerated wear test was devised. A machine originally developed at the National Bureau of Standards for measuring the relative wear of sole leather, and described in a former Bureau publication,[4] was changed in the Bureau's shops to adapt it for wear tests on traffic paint. A photograph of the machine is shown in figure 1, and a description of it and its method of use follows:

The wheel *A*,[5] 12 inches in diameter, carries a special rubber ring (⅜-inch thick) containing a uniformly distributed abrasive. When in use, it rests on and drives test panel *B* and is rotated at a speed of 1,600 revolutions per hour. The weight of the wheel and the portion of the machinery *G*, which it supports, is 40 pounds. The width of the rubber face on wheel *A* is 2 inches and the inner edge of the rubber ring is 4½ inches from the axis of *B*. The panel, *B*, is 15 inches in diameter and may be made of any suitable material, such as concrete, bituminous road material, or steel. In order to provide a greater shearing action, the freely moving turntable, *H*, supporting the panel *B* is provided with a brake, *C*, consisting of a brake wheel and a brake strap, by means of which any desired resistance to rotation may be secured by the application of dead weight. Hence, the abrading wheel travels at a greater speed than the test panel. For routine tests, it has been found unnecessary to use brake *C*, but it is used in experimental work. To keep the surface clean, a brush, *D*, and an exhaust fan, *E*, may be used.

All paints are now applied of the same wet film thickness (0.010 inch) by means of strips of shim steel and a straight edge, and the coat of paint is allowed to air-dry for 48 hours before putting it in the wearing-test machine. A single brushed coat of paint averages about 0.002 inch in thickness. However, traffic paints are applied in a thick coat, possibly about four to five times the thickness of the average brushed coat. After experimenting with various thicknesses ranging from 0.005 to 0.010 inch, the last one was selected for the test.

Likewise, the effect of drying the paint for varying periods, including 7, 18, 24, and 48 hours, was studied. One of the chief requirements of a traffic paint is that it shall dry rapidly (generally within 1 hour). However, it was found that the results of the accelerated wear test agreed more closely with the results of actual tests on roads, when the paint on the test panels was allowed to dry for 24 to 48 hours, than when the test panels had been dried for the shorter periods. For this reason, a drying period of 48 hours was selected for the accelerated test. All paint coats are dried at 25° C (77° F) and 50-percent relative humidity.

[3] The machine for testing the wear-resistance of traffic paints has been used since February 1934, and descriptions of it have been sent to several States and various individuals. A brief description, including a photograph of the machine, appeared in the 1935 and 1937 editions of Gardner's book entitled, "Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors."

[4] R. W. Hart and R. C. Bowker, *An apparatus for measuring the relative wear of sole leathers, and the results obtained with leather from different parts of a hide*, Tech. Paper BS 13 (1919). T147.

[5] A separable truck wheel purchased from Julius Fowl, Inc., 207 West 18th St., New York City. The tire was replaced by a rubber ring made by Eberhard Faber Rubber Co., 47 Golden St., Newark, N. J., of special eraser stock 1071.

A control paint of known durability on the road is always included when testing new materials.

Some of the results of the accelerated wear tests are shown in figures 2, 3, and 4. The same paints were used in figures 2 and 3, figure 2 showing results after 31 hours of wear (50,000 revolutions) and figure 3 after 51 hours of wear (80,000 revolutions). The same paint was placed on opposite sectors, so as to illustrate the uniformity of results. In other words, four paints were under test, of which V, the control paint, was the best, W next, C_B next, and C_D was the poorest. Paint V was made according to formula 2, given in the preceding section, and was very durable on the road. Figure 4 shows the uniformity of wear of two additional paints. These paints are on steel panels; concrete and asphalt panels are also used.

Bid samples (generally eight in number) are run at the same time with the control paint until the paints are worn badly. Generally, one or two paints show such superiority that the others are eliminated from consideration. The test is repeated, using only the paints which showed up well against the control. This elimination permits much larger areas to be painted for the final tests.

A paint film (0.010 inch thick) that shows practically no wear to the bare surface after 38,000 revolutions (about 24 hours) is considered to be a good wearing paint. A paint film that shows not over 50 percent of the area worn down to the bare surface after 50,000 revolutions is outstanding for wear resistance. Some traffic paints show as much as 50 percent wear after 10,000 revolutions. In some recent tests, particularly good resistance to wear was shown by two rubber-resin paints, formulated by different manufacturers. A third paint, supplied to the State of New York, a sample of which was received directly from the manufacturer, has shown unusually good resistance to wear on the machine. This paint contained powdered pumice and dried to a rough "sandy" finish which improves visibility at night. The same paint without the pumice dried to a smooth film and did not wear as well. A fourth sample, likewise embodying the rough-finish principle and representing material supplied to Pennsylvania, was also found to be a good-wearing paint in the machine.

The wearing test is still in the development stage, although the best-wearing paints on the road are generally the best in the accelerated tests. It must be remembered that, for paint under heavy traffic, resistance to abrasion is more important than resistance to weathering. A measure of the abrasion resistance may to a certain extent be indicated by the hardness of the paint coat, since the two properties are related. However, the hardest paint does not always wear the best, because the toughness of the paint film is an important factor. On the other hand, for paints on country roads, weathering and night visibility may be the more important factors.

A weathering cycle might, therefore, be introduced into the test. The following is suggested, the cycle to be repeated each day until badly worn paints are obtained:

9 a. m. to 3 p. m.—6 hours of carbon-arc light and water spray.
3 p. m. to 9 a. m.—18 hours of abrasion.
Wetting the panel during the wear test is not advisable because the film of water acts as a cushion, prolonging the test.

The conditions of service should be studied, and the accelerated tests made to fit these conditions. For example, the center-line stripe out on a country road is subjected to more weathering and less

FIGURE 1.—*Apparatus for testing abrasion resistance of traffic paints.*

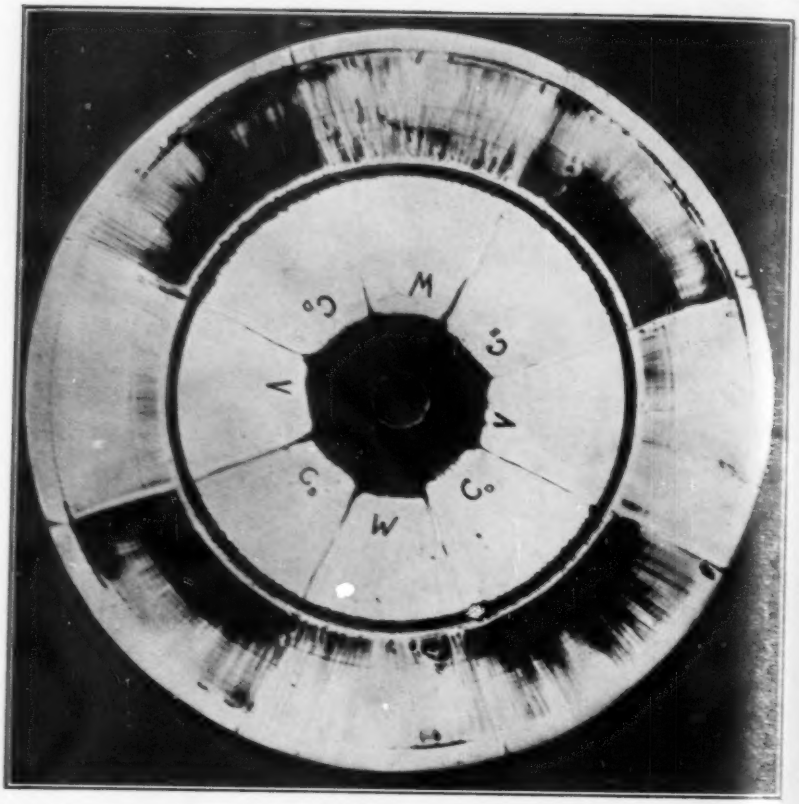

FIGURE 2.—*Appearance of four typical traffic paints after 50,000 revolutions in the testing machine.*

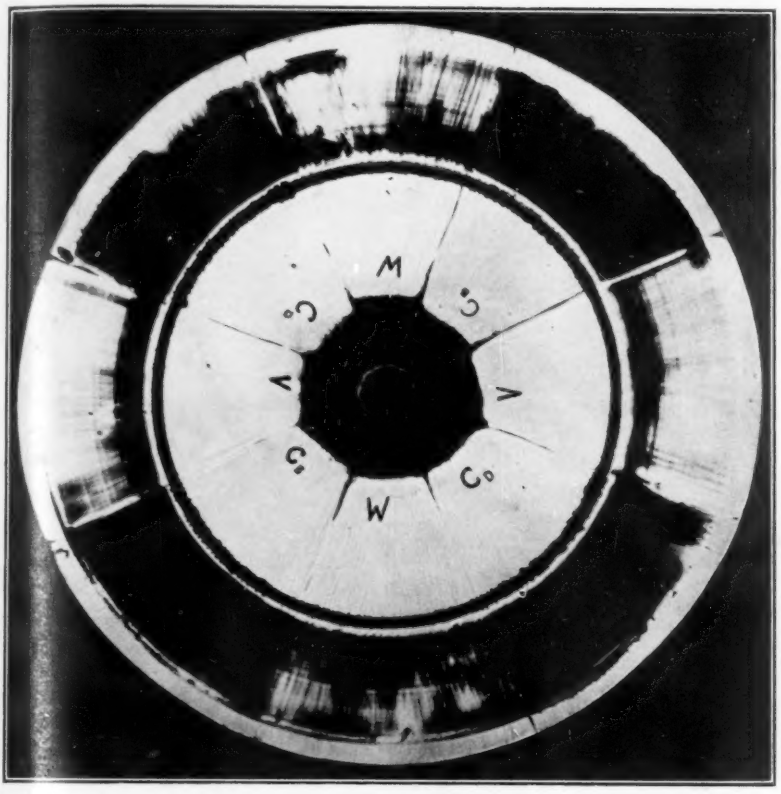

FIGURE 3.—*Appearance of four typical traffic paints after 80,000 revolutions in the testing machine.*

(The same paints after 50,000 revolutions are shown in fig. 2.)

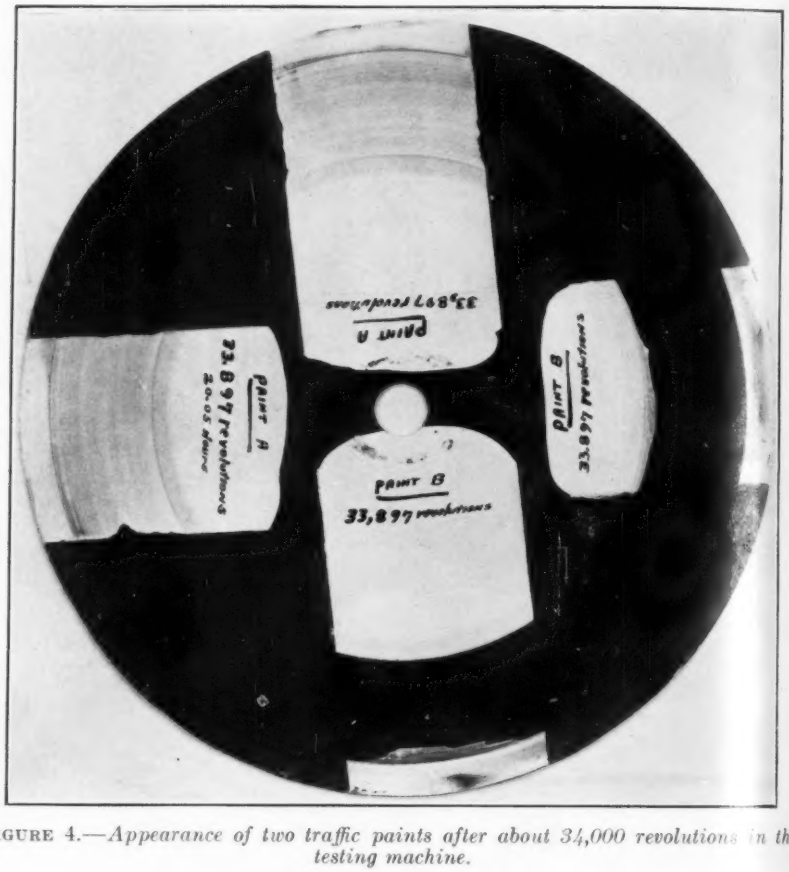

FIGURE 4.—*Appearance of two traffic paints after about 34,000 revolutions in the testing machine.*

(Note the uniformity of duplicate tests.)

abrasion than the stripes on the downtown streets of the city of Washington. Thus, in the former case, it might be advisable to expose the test panels to outdoor weather for a period of 10 days to 2 weeks before making the accelerated wear test. The wear test described in this paper was developed for *severe* traffic conditions.

V. SPECIFICATION FOR WHITE TRAFFIC PAINT

The following performance specification is being used at the present time by the District of Columbia in buying white traffic paint. The award is given the lowest-priced paint meeting the specification. Awards are not made by brands, and all paints are actually tested (both bid and delivery) before acceptance. The specification is based on work described in this publication, the accelerated service test being the one just described. The "control" paint, the formula for which is specified, was among the best of the experimental paints tried on the road. *Bidders do not have to make their paint according to this formula,* but the wear test must show their paint to be at least the equal of a paint properly made on this formula. It should be noted that the test paint has to pass not only the wear-resistance test, but the other tests in the specification also. The specification follows:

_____ gallons, paint, white traffic, ready-mixed, put in 5-gallon containers, with wire bail.

General.—All paint must be furnished in strong, substantial containers, plainly marked with lot number, name and address of manufacturer. The paint shall be well ground and mixed, shall not settle badly nor cake in the container, shall not thicken in storage to cause change in consistency, shall be readily broken up with a paddle to a uniform condition, capable of easy application with brush or mechanical distributor, in the ordinary manner according to the methods of standard practice. The paint is intended for use on bituminous or portland cement pavements.

Ready-mixed paint.—Ready-mixed paint, as received, shall be suitable for use with the usual paint brush or paint machine. It shall be well made, shall not "liver" nor settle badly, cake or thicken in the container within 3 months of delivery. It shall flow evenly and smoothly, and cover solidly in one coat on bituminous and portland cement pavements. It shall not cause the bitumen to "bleed" either during application or while it is drying. A single coat shall set in not less than 15 minutes nor more than 45 minutes (so that there shall be no pick-up under traffic) and *thoroughly* dry within 1½ hours, free from tackiness, to an elastic, opaque, adherent finish, when applied at temperatures between 40 and 90° Fahrenheit. It shall give a brilliant white finish, free from laps or brush marks. It shall not turn gray in sunlight, nor show appreciable discoloration with age. It shall show a wet hiding power of not less than 225 ft^2 per gallon (checkerboard brush-out method, ASTM Specification D 344–32T). It shall show a daylight reflectance of not less than 80 percent relative to that of magnesium oxide as the standard white (see National Bureau of Standards Letter Circular 395). The paint as received shall show a consistency of not less than 50 nor more than 200 seconds, using the Gardner Mobilometer with the 51-hole disk, a total moving load of 100 g, and a distance of 10 cm. (See Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors, by H. A. Gardner, 8th edition, page 590.) The paint furnished shall be at least equal, with respect to wearing properties, weathering, and water resistance, of a paint of the following composition:

Pigment	*Paint*
56 percent of titanium-barium pigment (not less than 25 percent of TiO_2).	Pigment 65 percent
24 percent of zinc oxide (American Process—lead free), for exterior use.	Vehicle 35 percent
20 percent of magnesium silicate.	

Liquid.—A properly cooked, quick drying, pale colored varnish, composed of drying oils, resins, drier, and volatile thinner. The oil portion is a mixture of

TABLE 1.—*Tests of white traffic paints*

Paint	1	2	3	4	5	6	7	8
Condition in can	Good	Good	Good	Good	Good	Good	Good	Settled badly.
Mobility, sec (25° C)	352	41	56	26	Over 600	21	Over 600	2.
Hiding power, ft²/gal	286	241	308	244	307	244	192	225.
Weight/gallon, lb	15.1	14.6	14.4	13.7	14.9	14.1	15.2	11.4.
Reflectance, percent	82	82	83	81	76	75	83	77.
Darkening of paint coat in strong light (6 hr carbon-arc)	None	None	None	None	None	None	None	None.
Bending test on nonvolatile vehicle [a]	O. K.	O. K.	O. K.	Slight cracking	O. K.	Cracked badly	O. K.	O. K.
Pigment, percent (by wt)	65.6	65.1	64.8	64.6	64.8	59.2	65.3	49.6.
Volatile, percent (by wt)	18.3	22.6	20.4	18.5	18.2	22.0	19.1	35.1.
Nonvolatile, percent (by wt)	16.1	12.3	14.8	16.9	17.0	18.8	15.6	15.3.
Nonvolatile vehicle, percent (by wt)	46.8	35.3	42.0	47.7	48.3	40.1	45.0	30.4.
Pigment analysis:								
Zinc oxide, percent	24.7	24.4	24.7	24.5	26.1	22.4	25.2	25.8.
Titanium oxide (TiO_2) percent	14.7	13.8	15.1	15.7	14.4	None	13.8	18.2.
Zinc sulphide, percent	None	None	None	None	None	18.7	None	None.
Barium sulphate, percent	Present	Present	Present	None	Present	Present	Present	Present.
Calcium	None	None	None	Present	None	None	None	None.
Siliceous	Present	Present	Present	Present	Present	Present	Present	Present.
Probable pigment composition:								
Zinc oxide, percent	25	25	25	25	26	22	25	26.
Titanium-barium pigment, percent	59	55	60	52 [c]	58	0	55	0.
Lithopone, percent	0	0	0	0	0	67	0	0.
Siliceous, percent	16	20	15	23	16	11	20	Balance. [d]
Set to touch, min (86° F)	10	10	15	35	30	15	25	15.
Dry—hours (86° F)	1	1	1¼	1½	1½	1¼	1¼	1.
Accelerated wear test [b]	Equal	Nearly equal	Equal	Below	Below	Below	Below	Equal.

[a] Air dry 30 minutes, bake 3 hours at 105° C, air dry 3 days, then bend over 3-mm rod at 25° C.
[b] Rating relative to "control" paint.
[c] Titanium-calcium pigment.
[d] Titanium oxide and inerts.

Paint	1	2	3
Composition of paint:			
Pigment, %	50	55	49
Volatile, %	24	30	28
Nonvolatile, %	26	19	23
Composition of vehicle:			
Volatile, %	48	58	55
Nonvolatile, %	52	42	45
Major pigment constituents: [a]			
Zinc oxide, %	15	16	16
Lead chromate ($PbCrO_4$), %	18	24	45
Insoluble in HCl, %	43	43	15
Zinc sulphide, %	None	None	None
Weight per gallon, lb	12	12.3	11.4
Odor	Mineral spirits	Benzol	Turpentine
Consistency	Paint	Thick paint	Paint
Mobility, sec.	50	193	51
Skinning in can	None	Skins	None
Brushing properties	Good	Slight pull	Good
Hiding power (wet), ft^2/gallon	256	269	375
Gloss	Eggshell	Flat	Semigloss
Color (compared to standard)	Lighter	More orange	Good (best match)
Drying properties:			
Set to touch, min	10	1	10
Dry firm	1½ hr	10 min	1½ hr
Hardness (after 24 hr. air drying)	Soft	Hard	Hard
Flexibility tests: [b]			
18 hr air dry	No cracks	No cracks	No cracks
2 hr carbon arc [c]	No cracks, no color change.	No cracks, no color change.	No cracks, no color change.
4 hr carbon arc [c]	do	Slight cracking, no color change.	do
6 hr carbon arc [c]	do	do	do
24 hr carbon arc [c]	do	Definite cracking, no color change.	Slight cracking slight darkening.
Accelerated wear test [d]	Equal	Equal	Better
Accelerated weathering, 48 hr air dry:			
Steel (one coat), 4 days	No cracks, best color retention.	No cracks, slight fading.	No cracks, very slight darkening.
Steel (one coat), 5 days	do	do	do
Concrete (one coat), 4 days	do	do	Blistered, very slight darkening.
Concrete (one coat), 5 days	do	do	do

[a] Remainder of pigments is essentially lead compounds other than chromate.

TABLE 2.—*Tests of yellow traffic paints*

3	4	5	6	7
	60	60	54	47
	28	22	20	25
	12	18	26	28
	70	55	44	47
	30	45	56	53
	16	15	17	17
	28	29	18	29
	43	41	42	42
	None	None	None	None
	13.1	13.5	12.8	12.2
ntine	Benzol	Benzol	Toluol	Benzol
	Thick paint	Paint	Livered in can	Thick paint
	255	62	Not determined	500
	None	None	Skins	None
	Slight pull	Slight pull	Bad pull	Slight pull
	337	291	Not determined	200
loss	Flat	Flat	Flat	Eggshell
(best match)	Much lighter	Fair (lighter)	Much lighter	Good
	5	5	5	5
	10 min	10 min	10 min	20 min
	Hard	Hard	Hard	Soft
acks	Fine cracking	Fine cracking	Definite cracking	No cracks
racks, no color nge.	Slight cracking, no color change.	Slight cracking, no color change.	Bad cracking, no color change.	Bad cracking, no color change.
o	Slight cracking, slight darkening.	do	do	Bad cracking, slight darkening.
o	do	Slight cracking, slight darkening.	do	do
cracking slight kening.	do	do	do	Bad cracking, definite darkening.
r	Worse	Worse	Equal	Better (best)
acks, very slight kening.	No cracks, very slight fading.	No cracks, definite fading.	Not determined	No cracks, slight fading.
o	do	do		do
red, very slight kening.	do	do	No cracks, slight fading.	Slight blistering, slight fading.
o	do	do	do	Bad blistering, slight fading.

[a] All bends made over ⅛-inch mandrel at 25° C.

[b] 18 hours air dry first.

	8	9	"Control" 10
	32	55	
	41	22	
	27	23	
	60	49	
	40	51	
	11	16	
	17	27	
	43	42	
	None	None	
	8.4	12.9	
	Benzol	Naphtha	
	Thin paint	Thick paint	
	2	450	
	None	None	
	Good	Slight pull	
	171	249	
	Eggshell	Flat	Flat.
	Too green	Too orange	White.
	5	5	10.
	15 min	15 min	1½ hr.
	Hard	Hard	Hard.
	Flakes from panel	No cracks	No cracks.
ng, no color	Flakes from tin, slight darkening.	Slight cracking, no color change.	Do.
ing, slight	do	do	
g.	Flakes from tin, definite darkening.	do	
ng, definite	do	Definite cracking, no color change.	
g. t)	Worst	Better	Used as standard.
slight fad-	Slight checking, definite darkening.	No checking, very slight darkening.	
ering, slight	Definite checking	do	
ring, slight	Slight blistering, definite darkening.	do	
	Definite blistering, definite darkening.	do	

ir dry first.

[4] Rating relative to "control" paint.

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properly cooked China wood oil and heat-bodied linseed oil, in the proportion of 60 parts china wood oil to 40 parts of linseed oil. The resin is a modified phenolic resin. The driers and volatile thinners are to give a quick-drying varnish, containing not less than 40 percent of nonvolatile matter. The varnish is 15 to 20 gallons in length (15 to 20 gallons of the above oils to each 100 pounds of the resin.)

Samples of paint submitted will be subjected to chemical analysis and test. The samples of paint will be applied on the pavement under field conditions and subjected to an *accelerated laboratory service test.* Comparative determinations of the rate of drying, amount of spread, resistance to discoloration, and durability will be noted.

VI. PROPERTIES OF WHITE PAINTS SUBMITTED UNDER THE SPECIFICATION

The results of examination of eight samples of commercial traffic white paints submitted under this specification are shown in table 1. The paints are arranged in order of increasing prices. The award was given paint 3. It is proving durable in actual service. Paint 1, while showing good wear, was too mobile to flow satisfactorily in the distributing machine.

VII. SPECIFICATION FOR YELLOW TRAFFIC PAINT

Recently, the District of Columbia desired to try (for the first time) some *yellow* traffic paint, in marking off street car-loading zones on bituminous roads. The National Bureau of Standards was asked to help in preparing a specification. It was suggested that the above-described specification for white traffic paint be used, except the hiding power be increased to a minimum of 250 ft^2, the color be light chrome yellow to match a standard, the paint to show good color retention when tested in the carbon-arc light, and the composition of the pigment to be specified as:

40 percent of (minimum) cp chrome yellow.
15 to 20 percent of zinc oxide (lead free), suitable for exterior use.
45 percent (maximum) of inert pigment (silica, china clay, magnesium silicate or a mixture).

In the accelerated wear test the white paint made on the suggested formula was still used as the "control."

VIII. PROPERTIES OF YELLOW PAINTS SUBMITTED UNDER THE SPECIFICATION

Table 2, showing the examination of nine yellow traffic paints submitted under this specification, may be of interest. It is to be noted that for information, some tests (flexibility tests, exposing panels to the carbon-arc light) were made other than those called for in the specification. The paints are arranged in order of increasing prices. The award was given paint 3. It is proving durable in actual service. Paints 1 and 2 failed to match the standard color.

The following manufacturers have contributed either raw materials, experimental paints, or suggestions:

Varcraft Works, Inc.
U. S. Gutta Percha Paint Co.
Monroe, Lederer & Taussig.
Industrial Paint Co.
Central Paint and Varnish Works.
Philadelphia Quartz Co.
Goodyear Tire and Rubber Co.
The Watson-Standard Co.
Hanline Brothers.
Baltimore Paint and Color Works.

J. C. McRae, division of materials, District of Columbia, cooperated closely with the author in this work. Clara Sentel and W. C. Porter, of the Bureau's paint laboratory, performed most of the analyses given in tables 1 and 2.

WASHINGTON, February 26, 1937.

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ARC AND SPARK SPECTRA OF LUTECIUM

By William F. Meggers and Bourdon F. Scribner

ABSTRACT

A new description of conventional arc and spark spectra of lutecium (cassiopeium) in the wave-length range 2000 to 11000 A has been completed. Wave-length measurements and intensity estimates are presented for 650 lines, 25 of which represent band heads presumably due to LuO, 250 are characteristic of neutral Lu atoms (Lu I spectrum), 370 of singly ionized atoms (Lu II spectrum), and the remainder probably belong to doubly ionized atoms (Lu III spectrum). These data should aid in the spectroscopic identification and analysis of lutecium and serve as a basis for further study of spectral structures, hyperfine structures, and Zeeman effects.

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I. INTRODUCTION

The chemical elements with atomic numbers 58 to 71, inclusive, known as the rare-earth group, are characterized by nearly identical chemical properties which prevent their complete separation or purification by chemical means [1].[1] Slight differences in physical properties permit partial separation from each other (by fractional crystallization or by electrolysis), but it is doubtful if any rare-earth element of *spectroscopic purity* has ever been available for study. Impure rare-earth materials, or misidentification of spectra, account for the mistaken discovery of new elements, such as demonium, by Rowland; incognitium and ionium, by Crookes; celtium, by Urbain; denebium, dubhium, eurosamarium, and welsium, by Eder [2].

The atomic-emission spectra of these elements are characterized, in general, by great complexity and considerable variability depending on the type of excitation. The complexity (aside from impurities) is due in part to large families of spectral terms, usually of high multiplicity [3], and in part to relatively low ionizing potentials [4] which result in the excitation of several successive atomic spectra in addition to rather complicated molecular spectra. The most extensive published descriptions of these spectra were made more than a quarter of a century ago by Exner and Haschek [5], and a tabulation of the number of lines they observed in arc and spark spectra gives some idea of the relative complexity of the spectra of rare-earth elements. See table 1.

[1] Numbers in brackets refer to literature citations at the end of this paper.

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TABLE 1.—*Number of lines published for rare-earth spectra by Exner and Haschek* [5]

Atomic number	Chemical symbol	Number of lines	
		Arc spectrum	Spark spectrum
58	Ce	2,894	1,758
59	Pr	2,490	1,732
60	Nd	2,762	2,540
61	Il		
62	Sm	1,679	1,085
63	Eu	857	1,508
64	Gd	1,687	1,401
65	Tb	2,487	1,379
66	Dy	3,312	1,464
67	Ho	1,482	1,222
68	Er	2,321	1,785
69	Tm	1,007	667
70	Yb	905	795
71	Lu	164	236

The past 15 years has been an epoch-making period for the development of the quantum theory and for the analysis of complex spectra, but the rare-earth group was the last to succumb to analysis. Taking advantage of the relative simplicity of Lu spectra, and guided by comparisons with theoretically similar spectra, the present authors succeeded in finding the first regularities [6], which were published in 1930. It was first necessary, however, to make new descriptions of the spectra since the older data were incomplete and unreliable. The purpose of the present paper is to make public, for purposes of spectroscopic identification, our complete description of the conventional arc and spark spectra of lutecium.

The first data published concerning Lu spectra consisted of 33 wave lengths (2701.8 to 3647.9 A) by Urbain [7] and 62 lines (2603.38 to 6222.6 A) by Auer von Welsbach [8], both of whom discovered the element practically simultaneously, the former naming it lutecium (Lu) and the latter cassiopeium (Cp). A little later Exner and Haschek [5] gave values for 164 arc lines (2392.26 to 6945.30 A) and 236 spark lines (2195.64 to 6463.38 A). Some information concerning lines characteristic of neutral and of ionized atoms may be gleaned from a comparison of these arc and spark tables, but the separation by means of these data is often false or ambiguous. In 1910 Eder and Valenta [9] published 48 lines (5476.94 to 7126.23) observed in the arc spectrum, and in 1911 gave reproductions of spectrograms [10], a table of 116 wave lengths for the arc spectrum (2390.84 to 7126.23 A) and 79 wave lengths for the spark spectrum (2603.38 to 6463.31 A). In 1915 Eder [11], having obtained a purer sample from Auer, published a new description of the arc spectrum listing 263 lines (2397.17 to 7237.89 A), but many of these are not now identifiable with Lu. Considering the briefness of published lists, the poor quality of early observations, the limited range of spectra, and the impure materials used, it must be admitted that the description of Lu spectra was in a very unsatisfactory state, and the necessity for making new observations before analysis of spectral structure could succeed is apparent. Our preliminary report on regularities in Lu spectra gave improved data for 100 classified lines [6]. A temperature classification of Lu spectra by King [12] lists 102 lines showing perfect agreement

with our separation of lines according to excitation stages. Incidentally, it may be added that the close coincidence of a strong Lu I line with the almost omnipresent Ca II line, 3968.47 A, noted by King, was mentioned 20 years earlier by Eder and Valenta [10.]

II. EXPERIMENTS

Our first measurements of Lu spectra were made in 1929 with a sample of lutecium oxide obtained from Eder 10 years earlier. It was part of his collection of rare earths prepared by Auer. This sample contained a considerable amount of Yb and some Tm, so that it was not possible to complete the description of Lu spectra without also investigating those of Yb and Tm. The Eder collection just referred to contained a sample of ytterbium oxide but lacked any specimen of Tm salt. The Yb was found to be contaminated with both Lu and Tm, so the identification of Lu and Yb lines could be effected, but considerable uncertainty remained about the removal of all Tm impurity lines from either Lu or Yb. When this situation was explained to Professor B. S. Hopkins, he kindly presented new samples of Lu, Yb, and Tm oxides prepared at the University of Illinois. With these materials we were able to check and extend our former lists of Lu and Yb lines, and also to make greatly improved descriptions of Tm spectra. This work was facilitated by the comparative purity of the Illinois samples. Although the Lu spectrograms show many Yb and some Tm lines, and the Tm spectrograms show both Yb and Lu, the best Yb sample is practically free of both Lu and Tm.

In order to insure the correct assignment of spectral lines to their origin, both as regards chemical element and stage of ionization, two procedures were followed: (1) The spectra of Lu, Yb, and Tm (and Er) were photographed side by side so that each line could be ascribed to the proper element on the basis of intensities, and (2) arc and spark spectra of each element were photographed in juxtaposition, so that intensity comparisons would separate lines from different excitation stages. In each case the rare-earth salt was fused on pure silver or copper electrodes for the production of arc spectra, and the identical silver electrodes were used in making spark spectrograms. Each pair of spectrograms was flanked by iron spectra for wave-length measurements, and the latter by blank spectra of the silver or copper. The arcs were operated with direct current of 5 amperes and applied potential of 220 volts, while the sparks were generated by high voltage (10,000 to 40,000) discharges from mica condensers of 0.006-microfarad capacity connected parallel with the spark in the secondary circuit of the transformers.

Ultraviolet spectrograms from 2000 to 3000 A were made with a Hilger E_1 quartz spectrograph. The interval 2500 to 8500 A was photographed with concave-grating spectrographs having either 15,000 or 20,000 lines per inch, while 7500 to 11000 A was studied with a similar grating spectrograph having 7,500 lines per inch. The dispersion values for the first-order spectra of the gratings are 5.0, 3.7, and 10 A/mm, respectively. Since only a fraction of a gram of each salt was used for making all the required spectrograms, it was imperative to get the maximum efficiency out of the spectrographs.

Hilger Schumann plates were used for the shortest waves, Eastman 33 plates covered the region 2300 to 4800 A, and sensitized plates (*EK* types *F*, *N*, *Q*) recorded the longer waves [13].

III. RESULTS

All wave-length measurements were made relative to iron standards (except 2000 to 2200 A, which was measured relative to copper standards), the values being those adopted by the International Astronomical Union [14], or those published by Burns and Walters [15]. Every line listed in table 2 was observed on two or more spectrograms (except a small number with questioned intensities observed only on strongest exposures). The stronger Lu lines were measured on 5 to 10 spectrograms, and many of them were measured an equal number of times on Yb and Tm spectrograms, where they appeared as impurities. The concordance of values from different spectrograms and the coincidence of wave lengths with impurity lines indicates that the final results for most lines are correct within 0.01 A, but errors of 0.02 A or more may exist among faint lines or those showing wide hyperfine structure. In some cases, it was difficult to decide if close lines represented fine or hyperfine structure, but our intention was to give only the center of gravity of complex lines. This hyperfine structure of Lu lines, first mentioned by the authors [6], was further commented on by King [12], and then studied in some detail by Schüler and Schmidt [16], and by Gollnow [17]. A nuclear moment of 5/2 was first announced [18] for 175 Lu, but this was later [16] increased to 7/2. Gollnow [17] reported the discovery of a new Lu isotope (mass number 173 or 177) whose relative abundance is estimated at 1.5 percent, and whose spin is 7/2 or possibly 9/2. Although the hyperfine structure of Lu lines is not resolved in our spectrograms, it widens some of the line images to 1 A or more, and may thus result in some uncertainty as to the centers of gravity and perhaps leads to overestimated intensities of wide lines. Some notes about *hfs* are given at the end of table 2.

Wave-length measurements and estimated relative intensities for 650 lines characteristic of Lu atoms are presented in table 2. About 250 of these lines belong to neutral atoms, 370 to singly ionized atoms, and 5 or 6 to doubly ionized atoms. In addition, some 25 band heads presumably due to LuO are given. Since spark spectra were not observed above 6800 A, the assignment of longer waves to I and II spectra is based principally on the term analysis of these spectra, and may possibly require some slight corrections when these analyses are completed. It is not unlikely that a few real Lu lines may have been discarded on account of coincidence with impurity lines, but the greatest deficiency in this description is probably in Lu spark lines masked by silver lines, or by air lines, and unobserved above 6800 A, unless they appear in the arc spectrum. The number of classified lines in Lu I and Lu II spectra has been increased to 200, but details of these analyses will be postponed until more complete and until Zeeman effects required for the interpretation of the spectral terms have been observed.

The strongest line characteristic of neutral Lu atoms is 6004.52 A, or possibly 4518.57 A, while the strongest line characteristic of singly ionized atoms is 5476.69 A with 6221.87 A and 6463.12 A next. It may be expected that the most intense lines will also be the most persistent or sensitive for detecting minute traces of Lu, so any sources in which neutral atoms predominate (flames, low-voltage arcs) should be examined for 6004.52 A, but if ionized atoms are most abundant

5476.69 A will reveal the lowest concentration of Lu. It appears that on account of the easy ionization of Lu atoms, the strongest Lu II lines have greater intensity than any Lu I lines in the ordinary 220-volt arc with short gap, and 5476.69 and 6221.87 A may be regarded as the most persistent lines of conventional arc and spark sources.

Attention is called to the fact that 19 of the 24 lines published by Urbain [19] as characteristic of "celtium" are now identified as lutecium.

TABLE 2.—*Arc and spark spectra of lutecium* ($Z=71$)

c=Complex, hyperfine structure (*hfs*).
d=Double, may be *hfs*.
e=Enhanced at electrode.
h=Hazy.
H=Very hazy.
l=Shaded or displaced to longer waves.
B=Band head.
p=Part of band structure.
I=Spectrum of neutral atoms.
II=Spectrum of singly ionized atoms.
III=Spectrum of doubly ionized atoms.
LuO=Molecular spectrum.

λ_{air} A	Intensity and character		Spectrum
	Arc	Spark	
2065.42	-------	30*h*	II
2070.66	-------	3*h*	II
2071.95	-------	2 Si?	II
2085.69	-------	5	II
2086.06	-------	2	II
2086.45	-------	4	II
2087.50	-------	5	II
2092.14	-------	6	II
2098.94	-------	1	II
2099.54	-------	10*h*	II
2100.40	-------	2	II
2101.32	-------	1	II
2104.40	-------	40	II
2107.84	-------	4	II
2109.14	-------	5	II
2110.22	-------	7	II
2110.37	-------	4	II
2117.14	-------	4	II
2117.82	-------	2 Yb?	II
2122.76	-------	6*h*	II
2124.13	-------	3 Yb?	II
2124.64	-------	2	II
2127.43	-------	4	II
2128.39	-------	5	II
2131.66	-------	6	II
2132.31	-------	5	II
2135.18	-------	5	II
2137.72	-------	8 Yb?	II
2139.19	-------	6	II
2139.76	-------	1	II
2140.53	-------	2*h*	II
2143.84	-------	3	II
2146.96	-------	2*h*	II
2147.59	-------	2*h*	II
2150.51	-------	2	II
2151.68	-------	1	II
2154.36	-------	7	II
2155.92	-------	3	II
2156.73	-------	4	II
2158.04	-------	2	II
2159.91	-------	2	II
2164.33	1	15	II
2173.30	-------	5 Yb?	II
2176.93	-------	4	II
2178.02	-------	8	II
2179.92	-------	1	II
2180.79	-------	5	II
2182.96	-------	1	II
2183.94	-------	1	II
2184.80	-------	6	II
2185.42	-------	2	II
2190.14	-------	6	II
2190.77	-------	4	II
2191.37	6	60	II
2194.80	-------	7	II
2195.54	30	100	II
2196.54	-------	2	II
2196.98	-------	4	II
2197.90	-------	2	II
2200.31	-------	6	II
2204.60	-------	2*h*	II
2206.82	-------	5*h*	II
2207.64	-------	2*h*	II
2216.70	-------	1	II
2217.32	-------	3*h*	II
2220.96	-------	1	II
2221.74	-------	2	II
2224.02	-------	6*h*	II
2236.17	6*d e*	150*h*	III
2239.39	-------	1	II
2249.53	-------	2*h*	II
2260.40	-------	4	II
2260.79	-------	2	II
2263.98	-------	3	II
2264.63	-------	2	II
2269.65	-------	1	II
2269.94	-------	1	II
2270.61	-------	4*h*	II
2270.95	-------	1	II
2271.97	-------	1	II
2276.94	8	20	II
2283.99	-------	3 Yb?	II
2291.74	-------	1	II
2293.34	-------	1	II
2293.78	-------	2	II
2297.41	15	100	II
2298.99	-------	1	II
2301.71	-------	1	II
2302.84	-------	1	II
2303.30	-------	2 Yb?	II
2306.38	-------	1	II
2307.54	-------	1	II
2310.66	-------	2*h*	II
2313.03	-------	5	II
2313.98	3	15*hl*	II
2322.61	-------	1	II
2333.04	-------	1	II
2333.41	-------	1	II
2334.38	-------	2 Yb?	II
2337.05	-------	3	II
2338.43	-------	1	II
2341.19	-------	3	II
2343.07	2	15	II
2345.50	-------	1	II
2348.60	-------	2	II
2349.14	-------	2*h*	II
2350.43	-------	3	II
2350.73	-------	1	II
2351.88	-------	2*h*	II
2352.76	-------	1	II
2357.28	-------	4	II
2359.38	-------	2	II
2363.18	-------	1	II
2367.77	-------	1	II
2368.22	-------	2	II
2369.08	-------	5	II
2380.57	-------	2	II
2381.69	-------	30*h*	II, III?
2385.20	-------	1	II
2387.45	-------	1	II
2388.69	-------	2	II
2390.23	-------	2	II
2392.19	30	100	II
2394.11	-------	1	II
2394.77	-------	1	II
2397.62	-------	1	II
2398.28	-------	1	II
2399.14	10	50	II
2401.58	-------	2	II
2403.69	-------	4*h*	II
2405.76	-------	1	II
2406.21	-------	2	II
2406.82	-------	2	II
2408.13	-------	1	II
2415.92	-------	5	II

See footnotes at end of table.

TABLE 2.—*Arc and spark spectra of lutecium (Z=71)*—Continued

λair A	Intensity and character		Spectrum
	Arc	Spark	
2419.21	8	40	II
2421.42	-------	4 Yb?	II
2421.97	-------	1	II
2424.90	-------	1	II
2427.21	-------	3	II
2430.26	3	15	II
2433.02	-------	1	II
2434.25	-------	2	II
2435.12	-------	1 Yb?	II
2445.83	-------	1	II
2449.75	-------	2	II
2449.96	-------	2	II
2451.60	-------	1	II
2454.87	-------	2	II
2455.60	-------	4	II
2456.50	-------	2	II
2457.56	-------	5h	II
2459.64	3	8	II
2463.95	-------	3	II
2464.82	5	?	I?
2467.68	-------	2	II
2469.27	10	40	II
2470.27	-------	1	II
2470.81	-------	1	II
2472.50	-------	2h	II
2475.34	-------	3	II
2481.72	20	100	II
2487.96	-------	4	II
2488.28	-------	1	II
2489.24	-------	2	II
2489.83	-------	2	II
2493.84	-------	2	II
2494.64	-------	6	II
2495.08	-------	1	II
2495.52	-------	2	II
2495.86	-------	1	II
2496.83	-------	2	II
2497.83	-------	2	II
2498.99	-------	3	II
2500.23	-------	1h	II
2500.86	5h	1	I
2509.04	-------	3 Tm?	II
2511.37	-------	1	II
2512.87	-------	2	II
2513.99	-------	1	II
2514.41	-------	1	II
2518.04	-------	4	II
2518.77	-------	1	II
2519.05	-------	1	II
2520.53	-------	2	II
2523.27	-------	1	II
2526.83	1	10h	II
2528.50	-------	5h	II
2529.84	-------	1	II
2530.55	-------	8h	II
2534.74	-------	2	II
2536.95	10	20	II
2538.12	-------	3 Yb?	II
2539.41	-------	1	II
2542.35	2	?	I?
2546.32	-------	5h	II
2546.87	-------	9h	II
2548.63	-------	10h	II
2549.52	20h	-------	I
2550.67	-------	3	II
2555.82	-------	2	II
2556.91	-------	2	II
2558.42	-------	6h	II
2561.80	-------	6h	II
2563.52	1e	80h	III
2571.23	30	100	II
2573.55	-------	2	II
2578.79	40	120	II
2582.13	3	20	II
2590.03	-------	3	II
2590.58	-------	2	II
2592.27	2h	?	I?
2592.34	-------	5h	II
2603.33 a	10d, e	300h	III
2607.32	-------	4h	II
2612.86	3h	?	I?
2613.40	30	100	II
2615.42	100	250	II
2619.26	30	100	II
2621.88	1	?	I?
2624.58	-------	1	II
2633.72	-------	2	II
2634.75	-------	1	II
2644.56	-------	2h	II
2652.48	-------	1	II
2653.34	-------	2h	II
2657.80	50	150	II
2660.46	-------	2	II
2670.78	5h	-------	I
2677.25	10h	-------	I
2677.77	1	10h	II
2685.08	50h	3	I
2685.54	10h	1	I
2688.09	-------	2	II
2692.34	5h	-------	I
2696.95	-------	2	II
2697.45	-------	2	II
2699.74	-------	3	II
2701.71	40	150	II
2703.13	7h	-------	I
2707.66	-------	1	II
2715.38	-------	1	II
2715.91	4h	-------	I
2719.09	10h	?	I
2724.81	-------	4	II
2728.95	40	2	I
2738.17	2	25hl	II
2749.70	-------	2hd?	II
2754.17	40	120	II
2765.74	20	3	I
2772.58	5e	150h	III
2778.52	-------	1	II
2781.47	4h	-------	I
2784.80	-------	8h	II
2785.70	-------	1	II
2787.44	-------	1	II
2796.63	25	100	II
2817.95	-------	1	II
2819.50	-------	6hl	II
2821.23	2e	50hl	III?
2826.82	-------	6hl	II
2828.95	-------	1	II
2829.42	-------	3h	II
2830.79	-------	1	II
2834.35	5	40h	II
2835.25	-------	10hd?	II
2845.13	30h	2	I
2845.87	-------	1h	II
2847.51	40	120	II
2855.36	-------	2	II
2860.31	-------	3	II
2860.94	-------	1	II
2862.74	-------	1	II
2863.61	-------	1h	II
2876.54	-------	2h	II
2879.02	-------	2h	II
2885.14	40h	3	I
2886.04	3	-------	I
2894.84	60	200	II
2900.30	50	150	II
2903.05	20	1	I
2905.92	-------	1	II
2911.39	100	300	II
2912.70	15h	-------	I
2920.69	-------	1	II
2923.37	-------	1	II
2931.53	7h	-------	I
2939.08	-------	2h	II
2946.39	-------	2h	II
2949.73	20h	1	I
2951.69	20	80	II
2955.78	2	60hl	II
2960.10	-------	2h	II
2963.32	50	150	II
2969.82	30	100	II
2975.67	-------	1	II
2978.50	-------	1	II
2985.85	-------	3h Yb?	II
2989.27	50	4	I
2992.48	-------	1	II
2995.84	-------	15hl	II
3003.65	-------	3h	II
3016.37	-------	15hl	II
3020.54	40	100	II
3027.29	4	8	II
3040.04	-------	20hl	II
3044.18	-------	1	II
3047.36	3h	-------	I
3055.70	1	2	II
3056.72	50	100	II
3057.90	3e	150h	III
3062.65	-------	2h	II
3063.51	20h	-------	I
3067.83	-------	3h	II
3077.60	100	200	II
3080.11	15	2	I
3081.47	80	8	I
3089.02	-------	8h	II
3101.99	-------	4hl	II
3104.98	-------	25hl	II
3115.32	2	1	I?
3118.43	40	5	I
3161.62	-------	10hl	II
3167.33	1	15hl	II
3171.36	40	5	I
3180.27	-------	1h	II
3183.73	3	6	II
3191.80	3	60hl	II
3198.12	40	80	II
3214.31	-------	1 Yb?	II

See footnotes at end of table.

TABLE 2.—*Arc and spark spectra of lutecium* ($Z=71$)—Continued

λ_{air} A	Intensity and character		Spectrum	λ_{air} A	Intensity and character		Spectrum	λ_{air} A	Intensity and character		Spectrum
	Arc	Spark			Arc	Spark			Arc	Spark	
3219.09	-------	3h	II	3829.07	10h	-------	I	4521.08	2h	-------	I
3222.57	-------	8h	II	3841.18	100	8	I	4525.48	2h	-------	I
3242.93	-------	4h	II	3843.61	15h	-------	I	4533.39	5*B*?	-------	LuO?
3245.93	-------	2h	II	3853.29	10	-------	I	4553.47	2*p*?	-------	I
3246.71	-------	2h	II	3870.88	5	-------	I	4560.95	8*Bl*	-------	LuO
3249.47	-------	4	II	3874.61	4	-------	I	4569.5	5*Bl*	-------	LuO
3251.95	-------	1h	II	3876.65	50c	100c	II	4575.31	5*Bl*	-------	LuO
3254.31	50	150	II	3888.38	-------	1h	II	4585.17	1*p*?	-------	I
3265.00	-------	10*hl*	II	3899.54	-------	3h	II	4586.93	2	6	II
3265.62	2	-------	I	3911.77	3h	-------	I	4590.68	3*B*?	-------	LuO?
3278.97	50	5	I	3918.86	4	-------	I	4602.04	1*p*?	-------	I
3280.50	10	-------	I	3925.30	20	1	I	4602.60	3h	-------	I
3281.74	60	5	I	3926.62	2	-------	I	4605.39	10h	-------	I
3303.75	-------	1h	II	3937.61	-------	5*hl*	II	4643.29	8h	-------	I
3305.68	2	? Yb?	I?	3968.46	50?	? Ca+	I	4645.47	25h	2	I
3312.11	100	10	I	3981.01	-------	2h	II	4648.21	25h	2	I
3319.63	-------	3h	II	3991.38	3	-------	I	4648.85	25h	?	I
3332.61	-------	8h	II	4030.86	-------	5*hl*	II	4651.94	2*p*?	-------	I
3338.62	-------	1	II	4033.02	4 Ga?	-------	I	4654.03	15*Bl*	-------	LuO
3359.56	150	15	I	4054.45	25	3	I	4656.49	2*p*?	-------	I
3364.26	-------	1	II	4079.87	1h	-------	I	4658.02	100	15	I
3376.50	100	10	I	4094.04	10*Bl*	-------	LuO	4659.03	10	1	I
3385.50	30	4	I	4096.13	20*Bl*	-------	LuO	4661.75	150*Bl*	15*Bl*	LuO
3391.55	10	2	I	4107.44	3*p*?	-------	I	4672.31	120*Bl*	12*Bl*	LuO
3396.82	30	1	I	4112.67	5	-------	I	4675.29	4*p*?	-------	I
3397.07	50	200	II	4122.49	15	2	I	4684.16	100*Bl*	10*Bl*	LuO
3418.42	3 Yb?	-------	I	4124.73	200	10	I	4689.77	4+*p*	-------	I
3423.30	-------	1h	II	4131.79	10+*p*	-------	I	4695.46	80*Bl*	8*Bl*	LuO
3464.77	-------	3h	II	4154.08	40	3	I	4708.00	60*Bl*	6*Bl*	LuO
3472.48	50	150	II	4158.98	1	-------	I	4716.70	5	-------	I
3491.92	-------	3h	II	4167.50	2	-------	I	4720.86	5*B*	-------	LuO
3507.39	100c	150	II	4184.25	100	200	II	4726.20	4*p*?	-------	I
3508.42	30	3	I	4223.09	1	4	II	4733.50	-------	3h	II
3518.89	1	-------	I	4223.99	2	-------	I	4735.00	25*Bl*	2	LuO
3521.18	3	-------	I	4235.51	1	-------	I	4748.38	-------	10*hl*	II
3525.94	2	-------	I	4239.30	5 Bl?	-------	LuO	4749.11	10*Bl*	1	LuO
3546.39	7	-------	I	4241.9	10*Bl*	-------	LuO	4757.26	1*p*?	-------	I
3553.10	2	-------	I	4252.53	5*B*?	? Yb+	LuO	4764.22	7*Bl*	1	LuO
3554.43	50	150	II	4262.02	-------	8	II	4774.05	1*p*?	-------	I
3567.84	100	7	I	4266.40	-------	2h	II	4779.00	1 Yb?	-------	I
3580.26	3	-------	I	4277.50	30	3	I	4780.11	5*B*	-------	LuO
3596.34	6	-------	I	4281.03	40	4	I	4785.42	100	200	II
3620.31	4	-------	I	4295.97	30	3	I	4798.00	3*B*	-------	LuO
3623.99	20	40	II	4296.09	15	2	I	4810.52	2 Zn?	-------	I
3628.90	2	-------	I	4309.57	25	2	I	4815.05	20	2	I
3636.25	25	3	I	4332.72	10	1	I	4839.62[b]	50c	100c	II
3642.35	2?	-------	I	4341.98	3	30*hl*	II	4843.03	2	5	II
3647.77	100	5	I	4355.05	3	-------	I	4844.44	3	-------	I
3678.04	-------	3h	II	4374.90	5	-------	I	4858.75	2	8	II
3682.40	1?	-------	I	4396.16	2	?	I?	4860.15	1h	-------	I
3684.32	15	1	I	4397.31	7	-------	I	4864.52	1h	-------	I
3704.79	-------	3h	II	4404.86	5?	-------	I	4865.36	4	20	II
3706.16	2	-------	I	4416.45	6	-------	I	4870.78	1h	-------	I
3710.95	3	-------	I	4420.96	15c	-------	I	4882.40	3h	-------	I
3722.58	3?	-------	I	4430.48	30c	2	I	4888.14	2h	-------	I
3724.32	2h?	-------	I	4438.79	4	-------	I	4895.00	1h	-------	I
3742.08	2	-------	I	4450.81	40	2	I	4904.88	60	5	I
3756.70	8	-------	I	4471.55	7	-------	I	4907.16	1h	-------	I
3756.79	6	-------	I	4480.15	3	-------	I	4911.41	1	-------	I
3777.15	-------	2h	II	4490.53	2	-------	I	4921.70	3	8	II
3786.18	4	-------	I	4498.85	10	1	I	4942.34	40	3	I
3793.24	4	-------	I	4505.22	1	5	II	4976.92	1h	-------	I
3800.67	5	-------	I	4508.91	5*B*?	-------	LuO	4994.13[c]	250c	400c	II
3802.62	3	-------	I	4517.71	1h	-------	I	5001.14	100	?	I
3814.02	2	-------	I	4518.57	300c	40	I	5057.60	15	1	I

See footnotes at end of table.

TABLE 2.—*Arc and spark spectra of lutecium (Z=71)*—Continued

λ_{air} A	Intensity and character		Spectrum	λ_{air} A	Intensity and character		Spectrum	λ_{air} A	Intensity and character		Spectrum
	Arc	Spark			Arc	Spark			Arc	Spark	
5134.05	20	2	I	6365.90[h]	25*d*	----------	I	8082.36	2	----------	I
5135.09	200	20	I	6441.14	40*c*	----------	I	8178.16	40*c*	----------	I
5161.06	4*Bl*	----------	LuO	6444.89	5	15	II	8248.68	2	----------	I
5170.11	10*Bl*	----------	LuO	6463.12[i]	400*c*	800	II	8329.45	5	----------	I
5196.61	10+*p*	----------	I	6477.67	30	2	I	8382.08	30	----------	I
5206.47	10	----------	I	6523.18	80*c*	5	I	8408.21	8	----------	I
5250.71	2*p*?	----------	I	6611.7[j]	100*c*	150*c*	II	8459.19	150	----------	II
5278.48	----------	2*h*	II	6619.15	5	----------	I	8478.50	50	----------	I
5304.40	20	2	I	6668.74	4*c*	----------	I	8508.08	100	----------	I
5349.12	25	2	I	6677.14	40	1	I	8610.98	120	----------	I
5402.57[d]	150*c*	10*c*	I	6735.76	5	----------	I	8690.23	3*h*	----------	I
5421.90	50*c*	5	I	6766.32	2*h*?	----------	I	8712.78	3	----------	II
5437.88	30	3	I	6793.77	40*c*	2	I	8719.00	1*e*	----------	I
5453.57	8	1	I	6826.59	4	----------	II	8744.03	3*e*	----------	I
5465.50	3?	----------	I	6892.55	3	----------	II	8788.83	4*e*	----------	I
5476.69[e]	500	1000	II	6917.31	50	----------	I	8795.6	2	----------	I
5505.91	1	----------	I	6943.96	5	----------	I	8949.5[m]	40*c*	----------	II
5602.56	1	5	II	7031.24	50	----------	I	9116.26	20*e*	----------	I
5664.89	2	20	II	7096.34	30*c*	----------	I	9203.92	8*e*	----------	I
5713.49	3	15	II	7101.98	2?	----------	I	9273.79	2*e*	----------	I
5736.55	150*c*	15	I	7125.84	120	----------	II	9282.5	1?	----------	I
5775.40	50	5	I	7142.79	7	----------	I	9504.50	2*e*	----------	I
5800.59	30	2	I	7143.10	5	----------	I	9661.69	10*e*	----------	II
5860.79	20*c*	2	I	7165.94	9	----------	II?	9696.03	30*e*	----------	I
5866.30	3	----------	I	7196.40	5*c*	----------	I	9841.32	2	----------	II
5887.23	1	6*h*	II	7229.06	2?	----------	I	9892.00	5*e*	----------	I
5961.39	3*e*	----------	I	7237.98	40*c*	----------	I	9909.9	1*e*?	----------	I
5983.9[f]	200*c*	400*c*	II	7324.97	2?	----------	I	9914.92	100*e*	----------	I
5997.13	50	5	I	7409.70	7	----------	II	10012.46	5*c*	----------	I
6004.52	400	40	I	7441.52	20	----------	I	10114.8	2*e*	----------	I
6041.66	20*c*	1	I	7456.96	5	----------	II	10118.54	4*e*	----------	I
6055.03	150*d*	10	I	7543.06	2	----------	I	10282.26	10*e*	----------	I
6084.14	15*c*	----------	I	7553.20	1	----------	I	10497.6	6	----------	I
6140.71	10*c*	----------	I	7640.08	9	----------	I	10680.5	8	----------	I
6141.72	5	----------	I	7649.54[k]	8*c*	----------	I	10729.8	10	----------	I
6159.94	50	200	II	7659.01	4*c*	----------	I	10758.2	5	----------	II
6195.12	15*c*	----------	I	7686.81	2*h*	----------	I	10770.2	20	----------	I
6199.66	40	120	II	7758.30	20*c*	----------	I				
6221.87[g]	500	1000	II	7815.9[l]	25*c*	----------	I				
6228.14	10	40	II	7911.62	30*c*	----------	I				
6235.36	25	100	II	7912.32	3?	----------	I				
6242.34	40	200	II	7917.52	15	----------	II				
6248.80	10*c*	----------	I	7927.58	2?	----------	I				
6345.35	60	4	I	7939.63	2	----------	I				
6354.85	20	1	I	7965.31	10*c*	----------	I				

[a] Measured double in arc {2603.28 (5).
2603.39 (5).

[b] Nine components according to Schüler and Schmidt [16].

[c] Thirteen components according to Schüler and Schmidt [16].

[d] Fifteen components according to Gollnow [17].

[e] Fifteen components according to Schüler and Schmidt [16].

[f] Seven components according to Schüler and Schmidt [16].

[g] Nine components according to Schüler and Schmidt [16].

[h] Measured double {6365.79 (10).
6366.00 (15).

[i] Three components according to Schüler and Schmidt [16].

[j] Five components measured {6611.28 (30).
6611.58 (25).
6611.80 (20).
6611.95 (15).
6612.04 (10).

[k] Diffuse double measured {7649.28 (3).
7649.79 (3).

[l] Unsymmetrical double measured {7815.84 (15).
7816.14 (6).

[m] Three components measured {8948.93 (20).
8949.63 (15).
8950.18 (10).

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CALIBRATION OF TESTING MACHINES UNDER DYNAMIC LOADING

By Bruce Wilson and Carl Johnson

ABSTRACT

The errors of the indicated loads of testing machines used to determine the mechanical properties of engineering materials are usually determined for static loads. Testing machines are often used to load specimens continuously to failure at a given rate of loading. The additional errors, due to rate of loading, of six testing machines comprising four types widely used in this country were determined by means of a special elastic calibrating device for rates of loading up to 50,000 lb/min. The additional errors in the indicated loads of these machines, due to rate of loading, at rates currently used in testing, exceeded in several cases the tolerances specified for such testing machines. These errors, therefore, cannot in general be neglected when determining the rates of loading to be used in materials testing. The results of these tests, although they cannot be used to correct the indicated loads of other testing machines of the same types because of small inherent differences in the weighing systems and slight differences of adjustment, are useful in that they indicate the magnitude of the errors to be expected.

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I. INTRODUCTION

The errors of the indicated loads of testing machines used to determine the mechanical properties of engineering materials are usually determined by methods of calibration involving the use of dead weights, standardized proving levers, or elastic calibration devices. These methods of calibration are included in the methods of calibration specified by the American Society for Testing Materials [1]. Each of these methods requires a constant or slowly increasing test load, while the calibrating device and the testing machine are read simultaneously. On the other hand, in materials testing, specimens are often loaded continuously to failure at a given rate of loading. The rate of loading for cement mortar cubes, for instance, may be as great as 6,000 lb/in.^{2}/min (24,000 lb/min for the standard cube)[2]. It is therefore important to know the magnitude of the errors of testing machines at the rates of loading used in testing. The additional errors due to rate of loading were determined for rates of loading up to 50,000 lb/min for six testing machines by means of a special elastic calibrating device. The six testing machines included one beam-and-poise, screw-driven machine; two pendulum, hydraulic machines; one spring, hydraulic machine; and two fluid-support, Bourdon-tube, hydraulic machines.

II. DESCRIPTION OF TESTING MACHINES

1. MACHINE *A*, BEAM AND POISE, SCREW-DRIVEN

The 50,000-lb capacity beam-and-poise, screw-driven machine, designated as machine *A*, is shown in figure 1. The load is applied to the specimen by the movable platen, *M*, which is moved by three screws. These screws are driven through gearing by an electric motor. The other platen, *N*, is supported upon a system of levers having knife-edge bearings. The lever system includes a graduated weigh beam, *O*, upon which a poise is moved manually, through gearing, by means of the hand wheel, *P*. When the beam is balanced, the magnitude of the load is indicated by the position of the poise on the beam. A vernier dial, graduated into 10-lb divisions, is provided to indicate fractional parts of the beam divisions.

Four different speeds of the movable platen, *M*, are obtainable by different gear combinations for a given motor speed. The motor speed can be controlled by means of multiple-step electrical resistances, *R*, so that the speed of the movable platen is almost continuously variable.

2. MACHINE *B*, PENDULUM, HYDRAULIC

The 50,000-lb capacity pendulum, hydraulic machine, designated as machine *B*, is shown in figure 2. The load is applied to the specimen by the movable platen, *M*, which is moved by a hydraulic jack which has no packing. This jack is connected hydraulically to two small jacks, the cylinders of which are rotated continuously to reduce friction. The pistons of the small jacks are connected mechanically to weighted pendulums by means of flexible steel straps. The force

[1] Am. Soc. Testing Materials Standards I, 849–860 (1936).
[2] Am. Soc. Testing Materials Tentative Standards, 393–398 (1936).

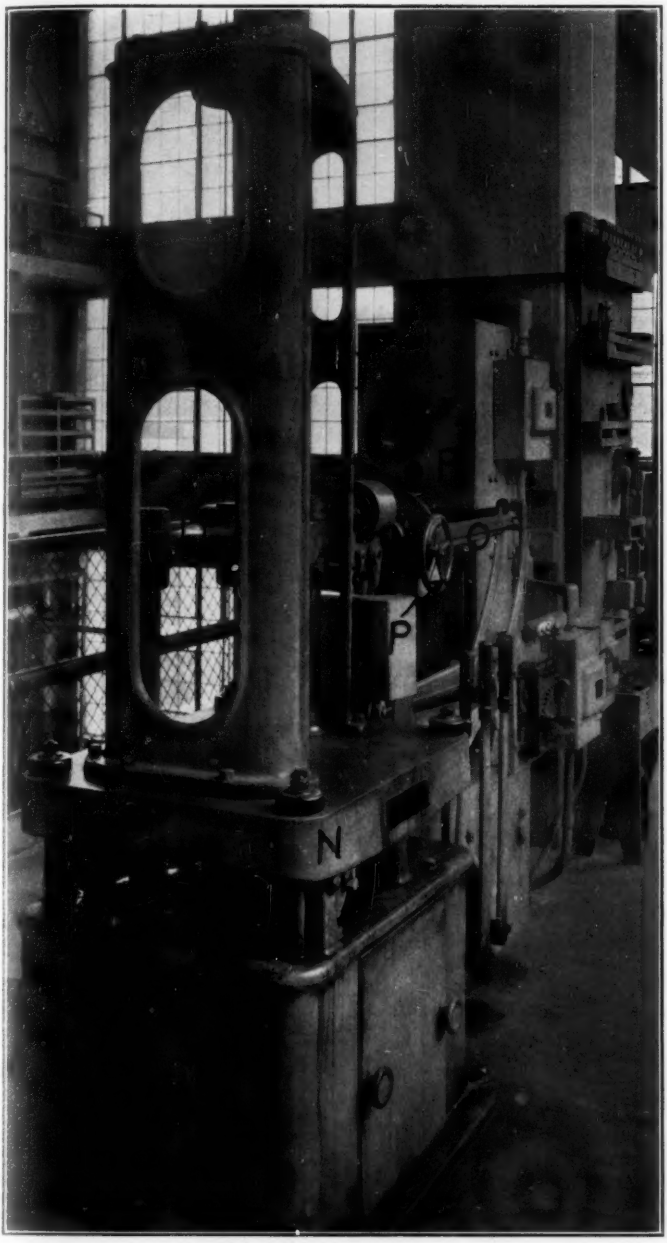

FIGURE 1.—*Machine A, 50,000-pound capacity beam and poise, screw-driven testing machine.*

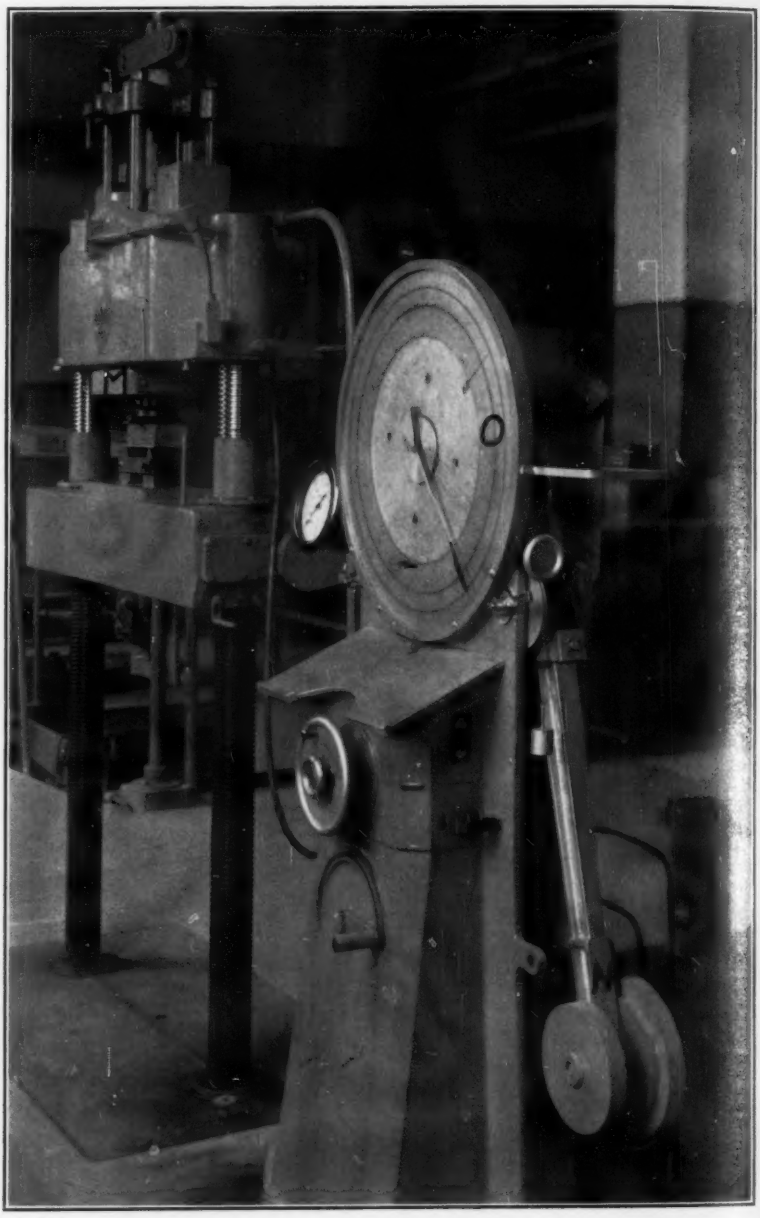

FIGURE 2.—*Machine B, 50,000-pound capacity pendulum, hydraulic testing machine.*

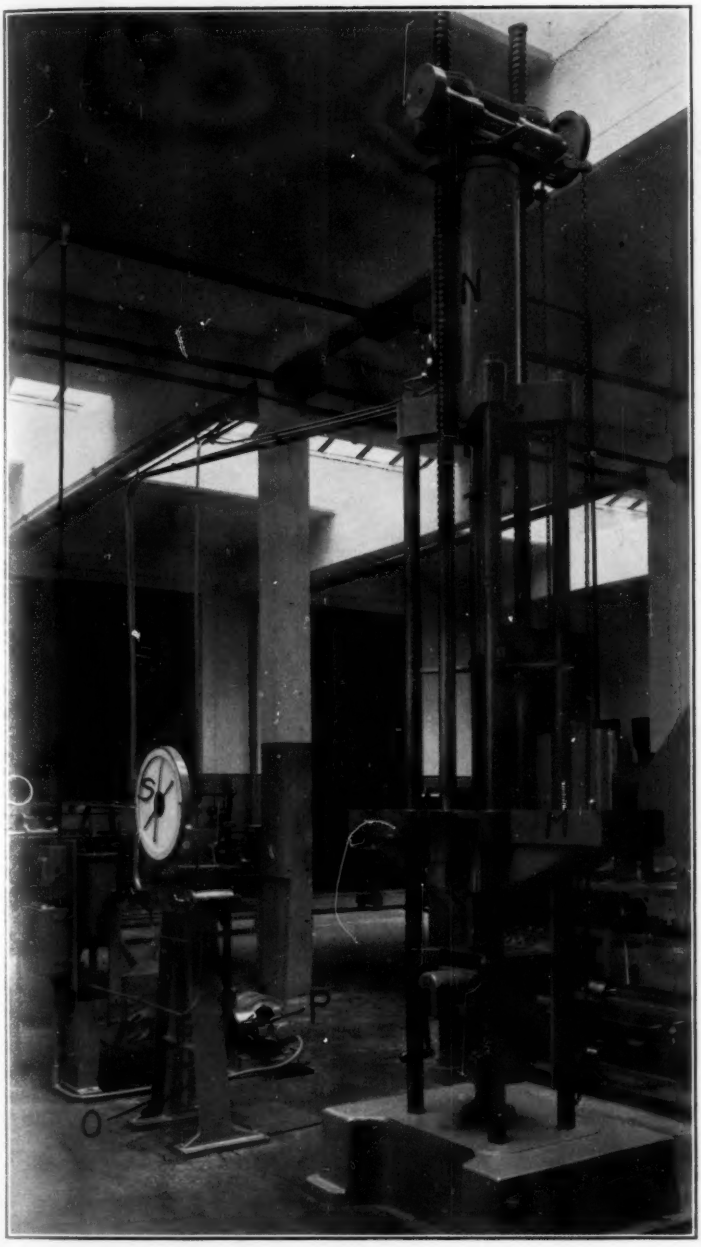

FIGURE 3.—*Machine C, 100,000-pound capacity pendulum, hydraulic testing machine.*

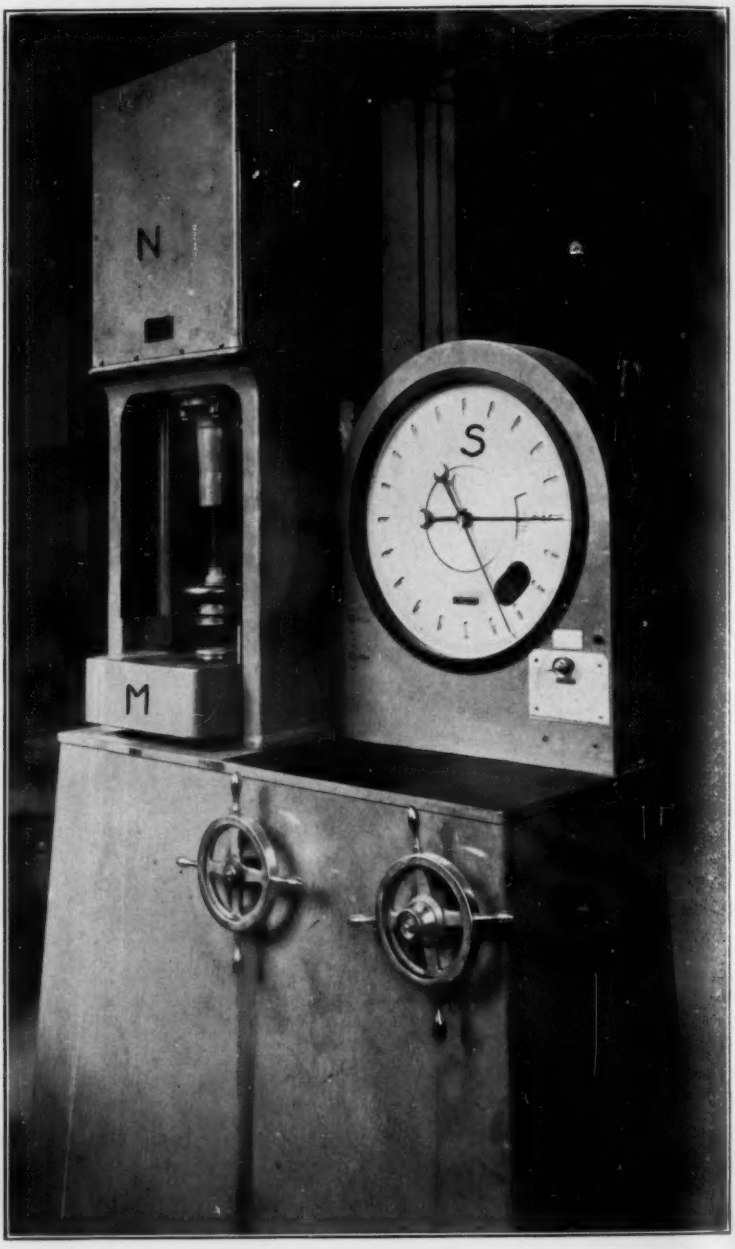

FIGURE 4.—*Machine D, 50,000-pound capacity spring, hydraulic testing machine.*

exerted by these pistons deflects the pendulums from their vertical positions. One of the pendulums, *N*, is shown in figure 2. Only one pendulum is used at a time. The pendulums are connected mechanically to a pointer which moves around a series of concentric graduated circular scales, *O*. The magnitude of the load is automatically indicated by the position of the pointer. A maximum pointer is provided to indicate the maximum load applied by the machine during a test.

This machine has scale ranges of 0 to 50,000 lb, 0 to 25,000 lb, 0 to 10,000 lb, and 0 to 5,000 lb. Tests were made using the 0- to 50,000-lb and the 0- to 10,000-lb scale ranges. These scale ranges are graduated into 50-lb and 10-lb divisions, respectively.

3. MACHINE *C*, PENDULUM, HYDRAULIC

The 100,000-lb capacity pendulum, hydraulic machine, designated as machine *C*, is shown in figure 3. The load is applied to the specimen by the movable platen, *M*, which is moved by a hydraulic jack, *N*, which has no packing. This jack is connected hydraulically to a small jack, *O*, the piston of which is rotated continuously to reduce friction. The piston of this small jack is connected mechanically to the weighted pendulum, *P*. The force exerted by the piston deflects the pendulum from its vertical position. The pendulum is connected mechanically to a pointer which moves around a graduated circular scale, *S*. The magnitude of the load is automatically indicated by the position of the pointer. A maximum pointer is provided to indicate the maximum load applied by the machine during a test.

This machine has scale ranges of 0 to 100,000 lb, 0 to 50,000 lb, 0 to 20,000 lb, and 0 to 10,000 lb. Tests were made using the 0- to 100,000-lb, 0- to 50,000-lb, and 0- to 10,000-lb scale ranges. These scale ranges are graduated into 100-lb, 50-lb, and 10-lb divisions, respectively.

4. MACHINE *D*, SPRING, HYDRAULIC

The 50,000-lb capacity spring, hydraulic machine, designated as machine *D*, is shown in figure 4. The load is applied to the specimen by the movable platen, *M*, which is moved by a hydraulic jack located inside the cover, *N*. This jack has no packing and its cylinder is rotated continuously to reduce friction. The loading jack is connected hydraulically to a small jack, the cylinder of which is rotated continuously to reduce friction. The piston of this small jack is connected mechanically to a pair of springs. The deflection of these springs is indicated by a pointer which moves around a graduated circular scale, *S*. The magnitude of the load is automatically indicated by the position of the pointer. A maximum pointer is provided to indicate the maximum load applied by the machine during a test.

This machine has scale ranges of 0 to 50,000 lb, 0 to 25,000 lb, 0 to 10,000 lb, 0 to 5,000 lb, and 0 to 2,500 lb. Tests were made using the 0- to-50,000-lb and the 0- to 10,000-lb scale ranges. These scale ranges are graduated into 50-lb and 10-lb divisions, respectively.

5. MACHINE *E*, FLUID-SUPPORT, BOURDON-TUBE, HYDRAULIC

The 100,000-lb capacity fluid-support, Bourdon-tube, hydraulic machine, designated as machine *E*, is shown in figure 5. The load is

applied to specimens by the movable platens, *M*, which are moved by a hydraulic jack, *N*, having a packing. The force exerted by the specimen on the other platen, *O*, is transmitted as a compressive force to a fluid support under the hydraulic jack. The fluid support, having a flexible diaphragm, is connected hydraulically to Bourdon-tube pressure gages, *P*. The pointers of these gages move around graduated circular scales. There is no hydraulic connection between the hydraulic jack and the fluid support. The magnitude of the load is automatically indicated by the positions of the pointers. Maximum pointers are provided on each gage to indicate the maximum load applied during a test.

This machine has scale ranges of 0 to 100,000 lb, 0 to 50,000 lb, and 0 to 10,000 lb. These scale ranges are graduated into 200-lb, 100-lb, and 20-lb divisions, respectively. Tests were made using each scale range.

In this machine there is a throttle valve in the line from the hydraulic support to each Bourdon-tube gage to reduce the rate of return of the pointer after a specimen is broken. Instructions furnished by the manufacturer state that this valve should be open one-eighth to one-fourth turn when a gage is in use. Tests were made using valve openings within this range and in some tests with greater openings. Since no specimens were being broken during these tests, there was no danger of damaging the gages by using openings greater than one-fourth turn.

6. MACHINE *F*, FLUID-SUPPORT, BOURDON-TUBE, HYDRAULIC

The 75,000-lb capacity fluid-support, Bourdon-tube, hydraulic machine, designated as machine *F*, is shown in figure 6. The load is applied to the specimen by the movable platen, *M*. The load-weighing mechanism of this machine is similar in principle to the load-weighing mechanism of machine *E*. In machine *F*, however, the fluid support is located between the piston of the loading jack and the lower platen, *M*. The fluid support is connected hydraulically to two Bourdon-tube gages, *P*. These gages have scale ranges of 0 to 75,000 lb and 0 to 10,000 lb and are graduated into 100-lb and 20-lb divisions, respectively. Maximum pointers are provided to indicate the maximum load applied during a test. Tests were made using both scale ranges.

This machine is equipped with ball-check valves instead of the throttle valves furnished on machine *E*. These valves are designed to allow a free flow of oil under increasing loads and a throttled flow of oil under decreasing loads. The manufacturer's instructions state that this type of check valve should be open one full turn when a gage is in use. In all of the tests made on machine *F* the valves were open one full turn.

III. METHOD OF CALIBRATION

1. ELASTIC CALIBRATING DEVICE

(a) DESCRIPTION

The elastic calibrating device is shown in figure 7. The device consists of a steel ring, *A*, which is loaded in compression through the integral external bosses, *B* and *C*. The diameter of this ring is ap-

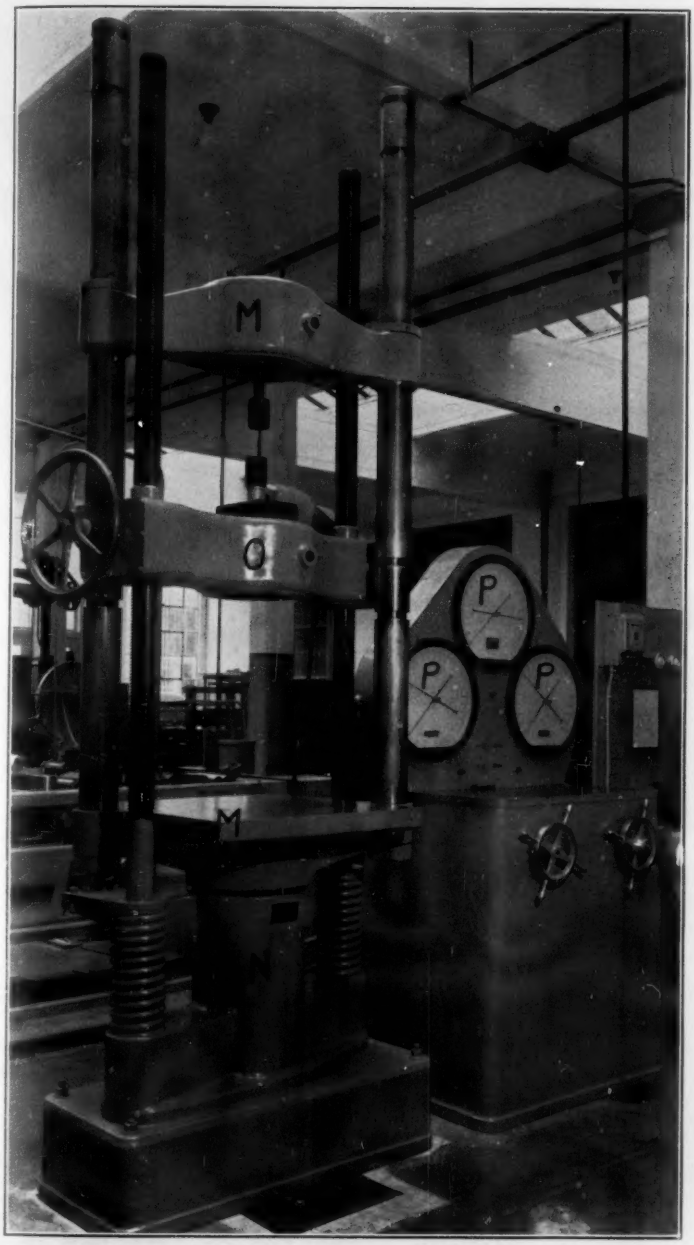

FIGURE 5.—*Machine E, 100,000-pound capacity fluid-support, Bourdon-tube, hydraulic testing machine.*

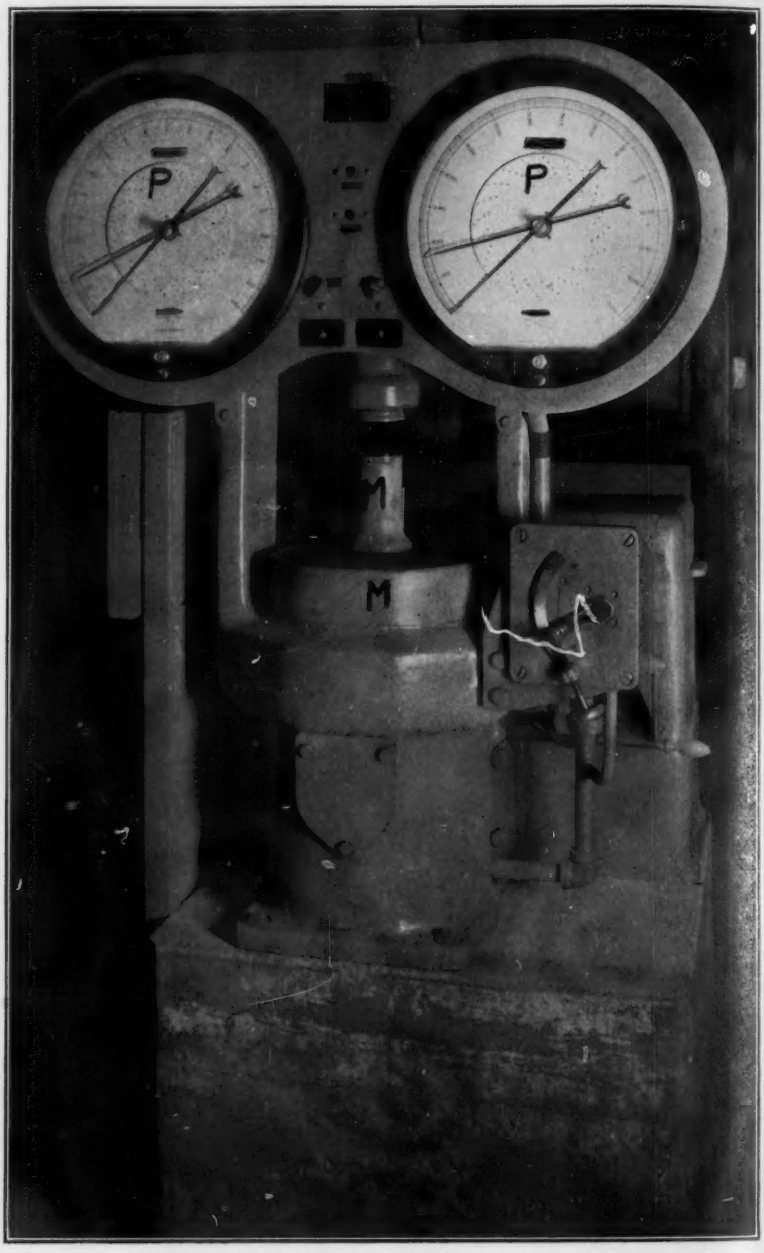

FIGURE 6.—*Machine F, 75,000-pound capacity fluid-support, Bourdon-tube, hydraulic testing machine.*

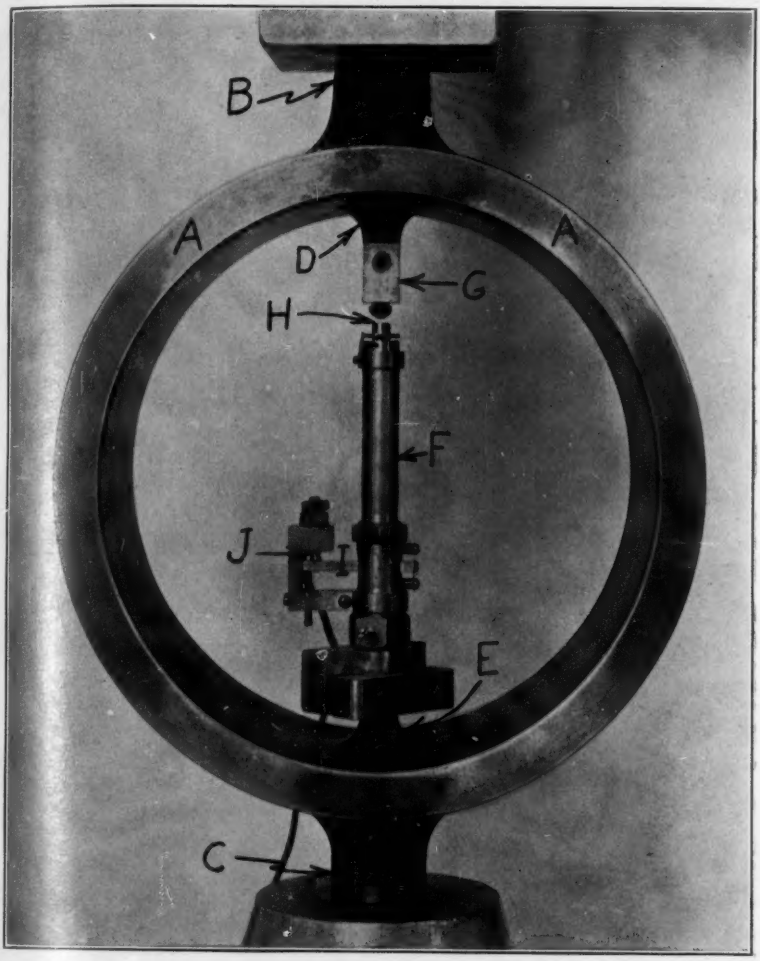

FIGURE 7.—*Elastic calibrating device, capacity 25,000 pounds.*

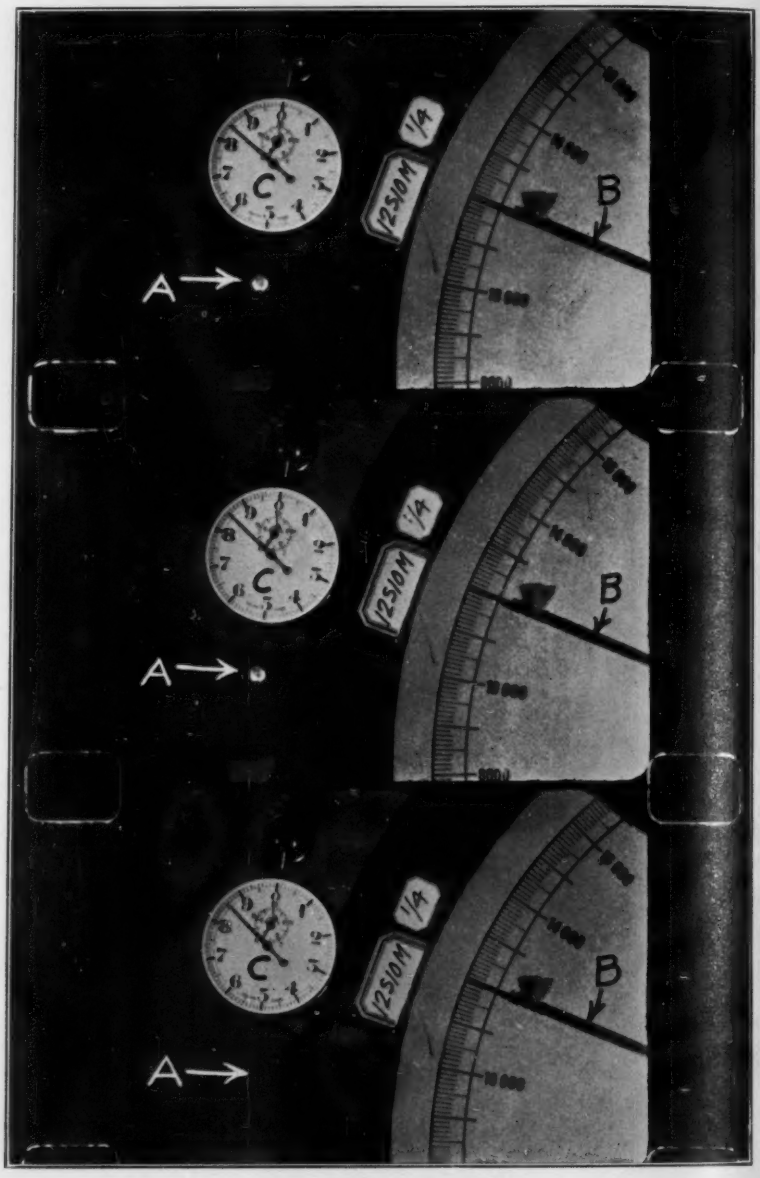

FIGURE 8.—*Reproduction of a strip of 16-millimeter film taken to record the dynamic reading of a testing machine.*

proximately 8 in. When a compressive load is applied to the ring, the loaded diameter shortens. This shortening can be measured by means of deflection measuring apparatus attached to the integral internal bosses, *D* and *E*. The deflection of the ring for its capacity load, 25,000 lb, was approximately 0.06 in. In these tests it was desired to have the elastic device indicate accurately when a given load had been applied to the ring. For this purpose the device was equipped with an electric contact, *F*, and an adjusting screw, *G*. The electric contact was devised by Charles Moon [3] of this Bureau. The electrical circuit of the contact is normally closed. When the ring is loaded so that the spherical head of the adjusting screw, *G*, pushes against the plunger, *H*, the lever, *I*, is actuated so that the electrical circuit is broken at the contact points, *J*. In these tests the contact was connected in series with a neon glow lamp and a source of direct current. When the device was in use the lamp would glow until the applied load for which the device had been set was reached. When this load was reached, the lamp would cease to glow.

(b) SENSITIVITY

Tests to determine how closely the elastic calibrating device would indicate a given applied load were made by loading the device with dead weights. These tests showed that the elastic calibrating device was sensitive to less than 2 lb for any load not exceeding the capacity load of the device.

(c) ERROR DUE TO INSTANTANEOUS TEMPERATURE EFFECT

The static load required to cause the lamp to cease to glow for a given adjustment of the elastic calibrating device, theoretically differs slightly from the dynamic load because of an instantaneous temperature effect. This error for proving rings was considered by L. B. Tuckerman [4] in his discussion of a paper by M. F. Sayre.[5] Calculations show that for the device used in these tests the error attributable to instantaneous temperature effect did not exceed 2 lb.

2. TESTING-MACHINE INDICATED LOADS

(a) STATIC

The indicated loads of the testing machines for a given adjustment of the elastic calibrating device were obtained under static conditions by reading directly the loads indicated by the machines at the instant the lamp ceased to glow. These readings were taken under very slowly increasing loads, but they will be referred to as "static" readings.

(b) DYNAMIC

The indicated loads of the testing machines for "dynamic" loading were obtained by photographing the lamp and parts of the testing-machine scales with a motion-picture camera. In each case the indicated load of the testing machine, read from the first frame of the film on which the lamp did not show, was taken as the dynamic reading of the machine for the rate of loading used. Camera speeds of 16, 32, and 64 frames per second were used.

[3] J. Opt. Soc. Am. & Rev. Sci. Instr. **11**, 453–458 (1925).
[4] Proc. Am. Soc. Testing Materials **32**, II, 594–606 (1932).
[5] Proc. Am. Soc. Testing Materials **32**, II, 584–592 (1932).

The dynamic reading was greater than the actual indicated load of the testing machine at the instant the lamp ceased to glow due to the motion of the pointer between the instant the lamp ceased to glow and the time the next exposure was made. Calculations show that this error did not exceed 25 lb for the camera speeds and the rates of loading used.

Figure 8 shows three successive frames of film taken during a test on one of the machines. The lamp, *A*, can be seen in the two upper frames. The lamp had ceased to glow before the lower frame was exposed. The reading indicated by the pointer, *B*, in the lower frame was taken as the dynamic reading. The watch, *C*, was used to determine the rate of loading.

3. RATES OF LOADING

Two methods were used during these tests to determine the rates of loading of the testing machines.

For all tests except those made with the 0- to 50,000-lb scale ranges of machines *B* and *D* the rates of loading of the testing machines were determined from measurements of the time required to increase the load from 1,000 lb below to 1,000 lb above the load for which the elastic calibrating device was adjusted. This time was measured with a stop watch graduated to 0.1 second. For the tests made with the 0- to 50,000-lb scale ranges of machines *B* and *D*, a metronome was used to give audible signals at predetermined intervals of time and the operator adjusted the controls of the testing machines to maintain the desired rates of loading.

4. TESTING PROCEDURE

The elastic calibrating device was preloaded in the testing machine. The device was then adjusted so that the lamp ceased to glow at the desired static reading of the testing machine. Alternate static and dynamic readings were then taken, with this adjustment of the device, for different rates of loading up to approximately 50,000 lb/min (50 kips/min). Both static and dynamic readings were taken with and without the maximum pointers for all machines except machine *A*, which does not automatically indicate the load. In each case the readings taken with the maximum pointer were obtained with both pointers moving together and the readings taken without the maximum pointer were obtained after the maximum pointer had been previously advanced out of range. The errors due to rate of loading both with and without the maximum pointers were obtained by subtracting the static readings taken without the maximum pointer from the dynamic readings. The total error in the indicated load of a testing machine would be the algebraic sum of the error for static loads and the additional error due to rate of loading.

IV. RESULTS OF TESTS

1. MACHINE *A*

Machine *A* does not automatically indicate the magnitude of the load. The operator must move the poise to keep the beam balanced during the application of load. In order to determine the error due to rate of loading, two series of tests were made. In the first series of tests the operator kept the beam balanced to the best of his ability

and the dynamic readings were recorded photographically. Since, in testing specimens, the indicated load of the testing machine is read after the operator has stopped moving the poise, a second series of tests was made to determine the error due to overrunning the poise.

The results of the tests in which the indicated loads of machine *A* for dynamic loading were obtained photographically are shown in figure 9. For each rate of loading readings were taken at 6, 13, and 18 kips, as indicated on the graph. The points show a considerable scatter above and below the 0-error axis, the scatter increasing with the rate of loading. This scatter is due primarily to the inability of the operator to keep the beam accurately balanced. Any error due

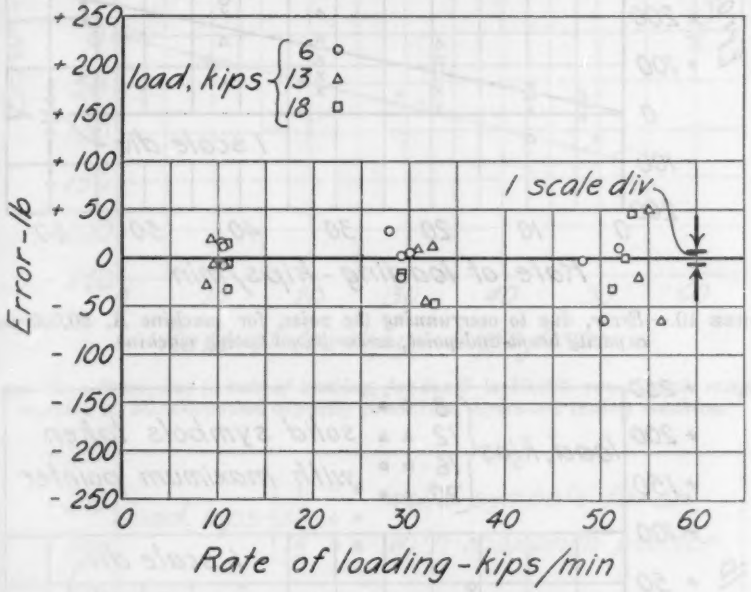

FIGURE 9.—*Error, due to rate of loading, for machine A, 50,000-pound capacity beam-and-poise, screw-driven testing machine.*

to rate of loading is so small that it is completely masked by the errors caused by the beam not being balanced.

In the second series of tests the lamp was placed near the trig loop of the machine and the operator stopped turning the handwheel, *P*, figure 1, as soon as possible after the lamp ceased to glow. The indicated load of the testing machine was read after the operator had stopped moving the poise. The results obtained by three experienced operators are shown in figure 10. Although there is considerable scatter of the points because of the inability of the operators to keep the beam balanced, there is a tendency on the part of each operator to overrun the poise. The average error due to overrunning the poise appears to be almost directly proportional to the rate of loading.

2. MACHINE *B*

The results of the tests made on machine *B* are shown in figures 11 and 12.

The results shown in figure 11 for the 0- to 50,000-lb scale range indicate that any error due to rate of loading is so small that it is

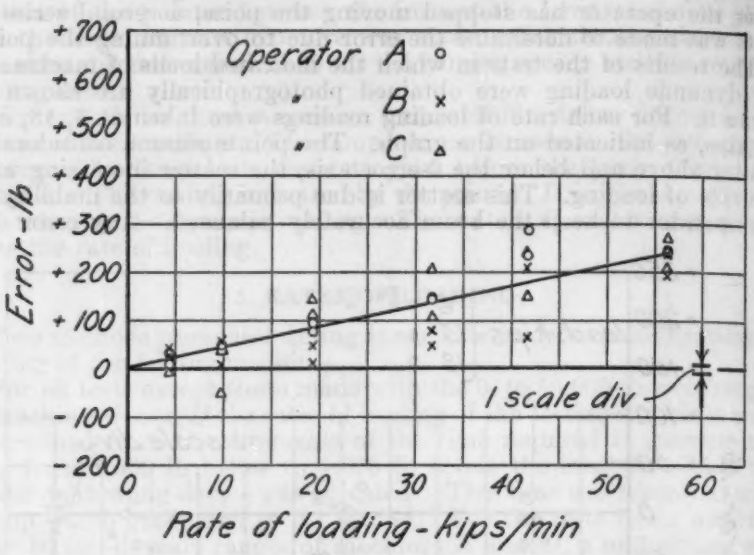

FIGURE 10.—*Error, due to overrunning the poise, for machine A, 50,000-pound capacity beam-and-poise, screw-driven testing machine.*

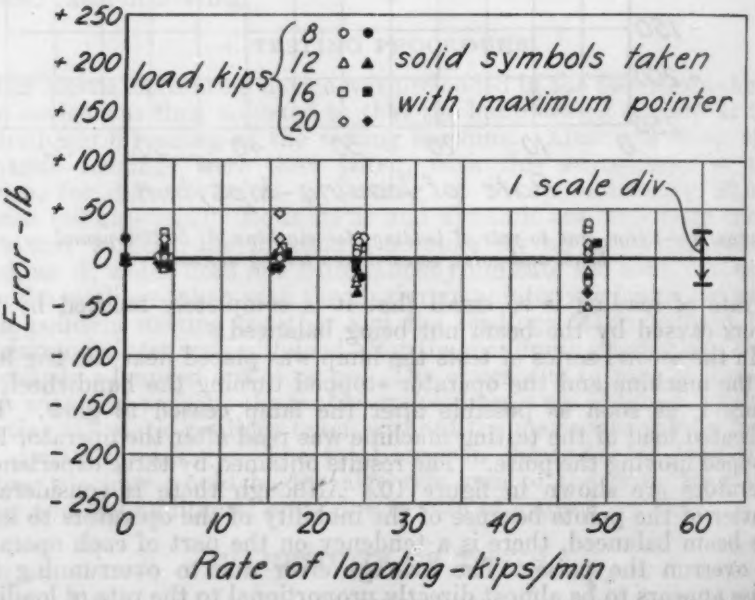

FIGURE 11.—*Error, due to rate of loading, for the 0- to 50,000-pound scale range of machine B, 50,000-pound capacity pendulum, hydraulic testing machine.*

completely masked by the scatter of the individual points. This scatter is caused by the fact that the machine does not indicate the same load for repeated applications of the same load. There appears

to be practically no additional error due to the use of the maximum pointer.

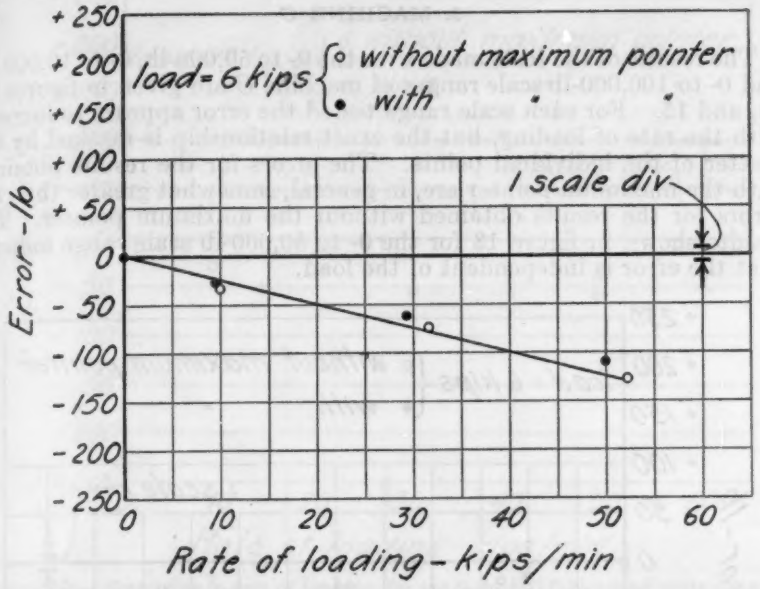

FIGURE 12.—*Error, due to rate of loading, for the 0- to 10,000-pound scale range of machine B, 50,000-pound capacity pendulum, hydraulic testing machine.*

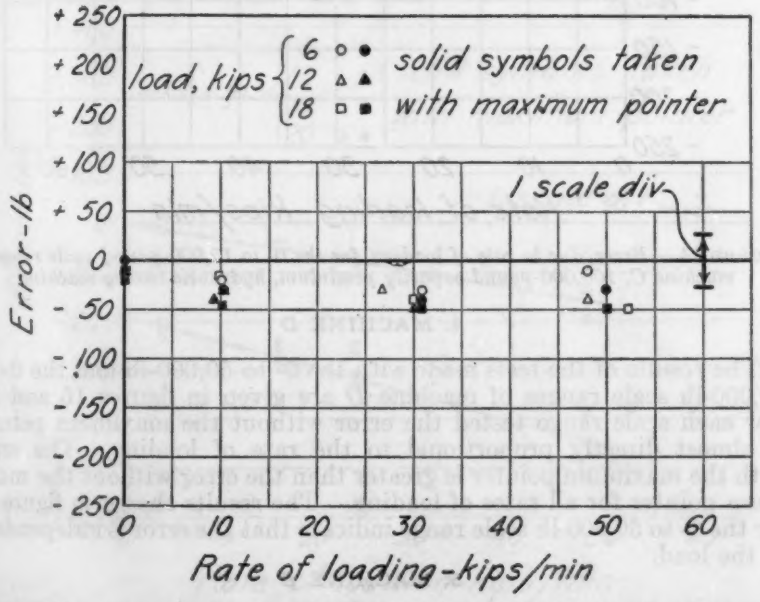

FIGURE 13.—*Error, due to rate of loading, for the 0- to 50,000-pound scale range of machine C, 100,000-pound capacity pendulum, hydraulic testing machine.*

The results given in figure 12 for the 0- to 10,000-lb scale range show that the error is almost directly proportional to the rate of loading.

There is little difference between the results obtained with and without the maximum pointer.

3. MACHINE *C*

The results of the tests made with the 0- to 50,000-lb, 0- to 10,000-lb, and 0- to 100,000-lb scale ranges of machine *C* are given in figures 13, 14, and 15. For each scale range tested the error appears to increase with the rate of loading, but the exact relationship is masked by the scatter of the individual points. The errors for the results obtained with the maximum pointer are, in general, somewhat greater than the errors for the results obtained without the maximum pointer. The results shown in figure 13 for the 0- to 50,000-lb scale range indicate that the error is independent of the load.

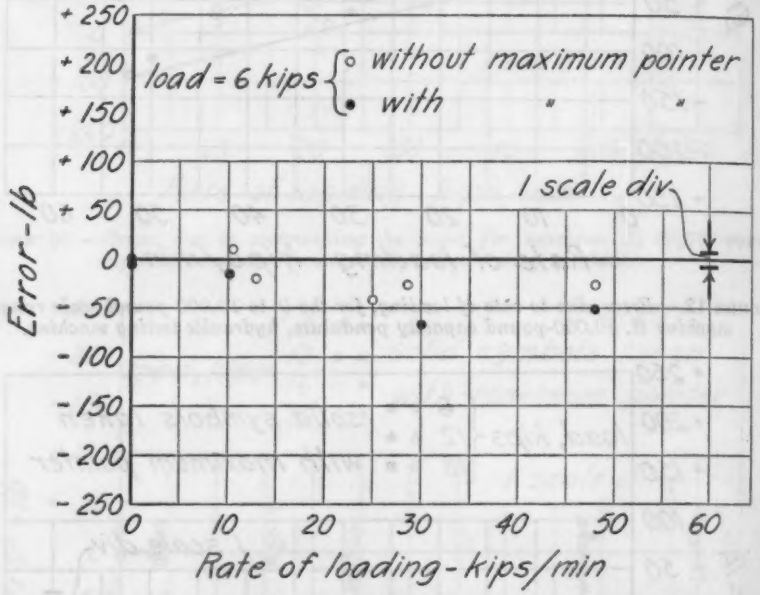

FIGURE 14.—*Error, due to rate of loading, for the 0- to 10,000-pound scale range of machine C, 100,000-pound capacity pendulum, hydraulic testing machine.*

4. MACHINE *D*

The results of the tests made with the 0- to 50,000-lb and the 0- to 10,000-lb scale ranges of machine *D* are given in figures 16 and 17. For each scale range tested the error without the maximum pointer is almost directly proportional to the rate of loading. The error with the maximum pointer is greater than the error without the maximum pointer for all rates of loading. The results shown in figure 16 for the 0- to 50,000-lb scale range indicate that the error is independent of the load.

5. MACHINE *E*

The results of the tests made with the 0- to 50,000-lb, 0- to 10,000-lb, and 0- to 100,000-lb scale ranges of machine *E* are shown in figures 18, 19, and 20.

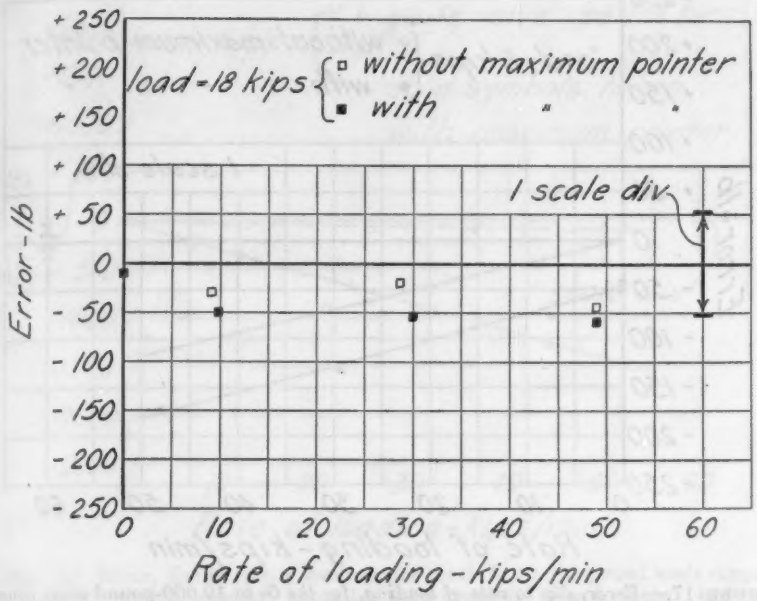

FIGURE 15.—*Error, due to rate of loading, for the 0- to 100,000-pound scale range of machine C, 100,000-pound capacity pendulum, hydraulic testing machine.*

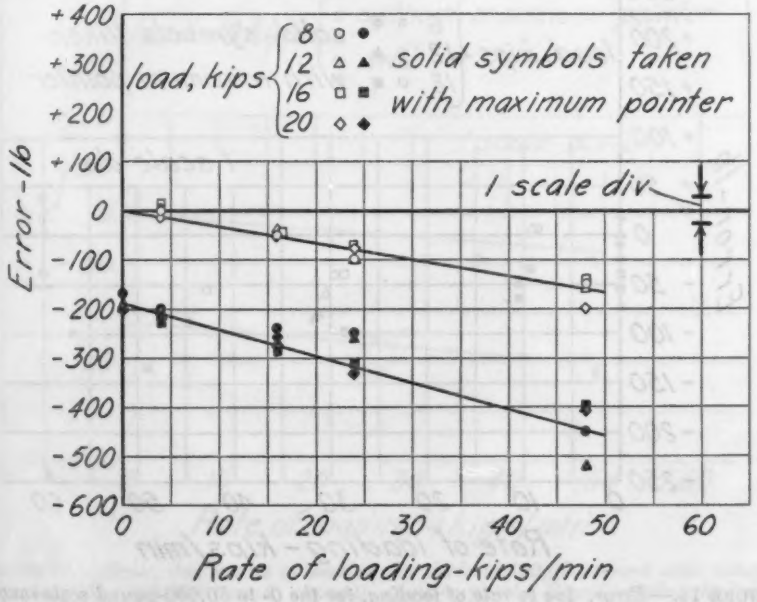

FIGURE 16.—*Error, due to rate of loading, for the 0- to 50,000-pound scale range of machine D, 50,000-pound capacity spring, hydraulic testing machine.*

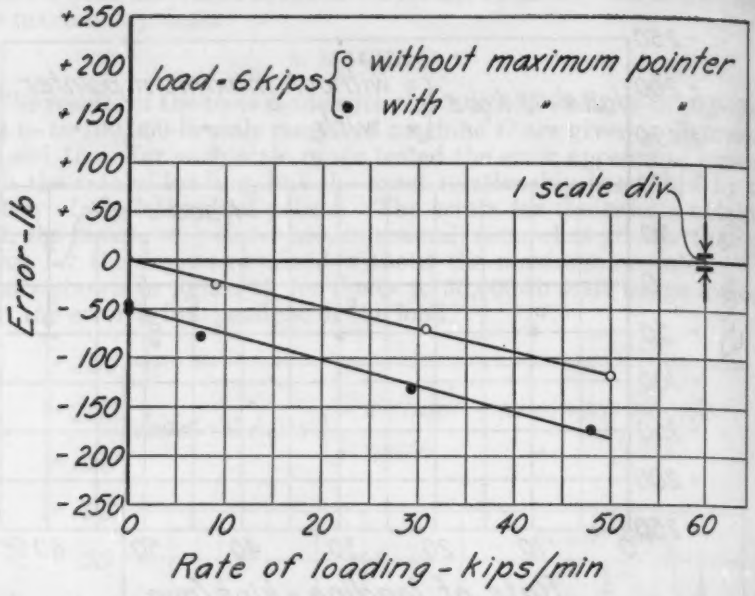

FIGURE 17.—*Error, due to rate of loading, for the 0- to 10,000-pound scale range of machine D, 50,000-pound capacity spring, hydraulic testing machine.*

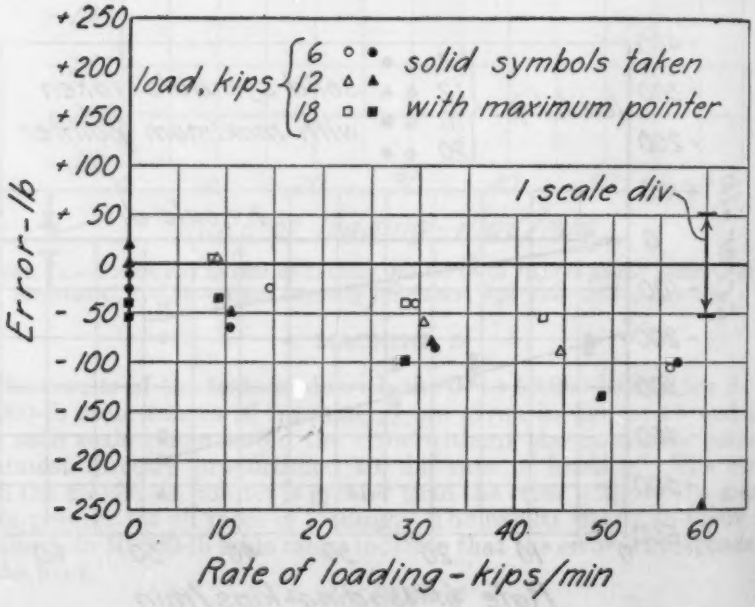

FIGURE 18.—*Error, due to rate of loading, for the 0- to 50,000-pound scale range of machine E, 100,000-pound capacity fluid-support, Bourdon-tube, hydraulic testing machine.*

[Gage throttle valve open one-fourth turn.]

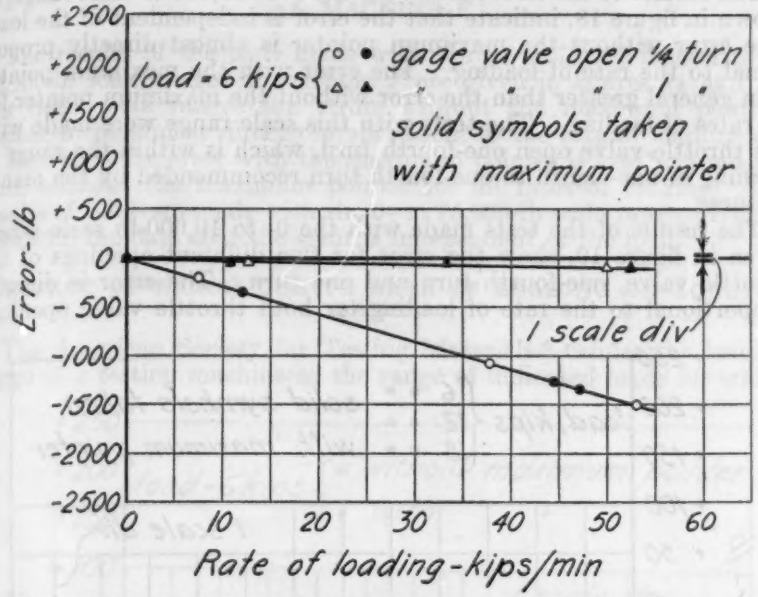

FIGURE 19.—*Error, due to rate of loading, for the 0- to 10,000-pound scale range of machine E, 100,000-pound capacity fluid-support, Bourdon-tube, hydraulic testing machine.*

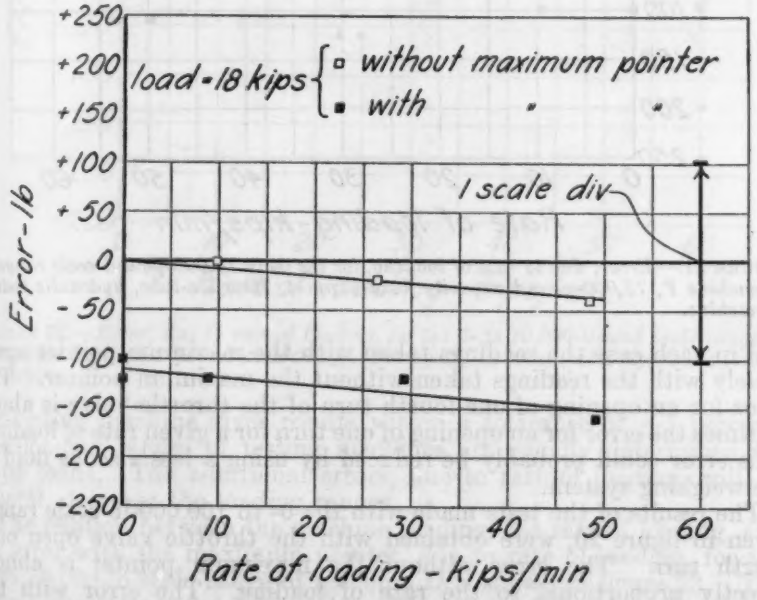

FIGURE 20.—*Error, due to rate of loading, for the 0- to 100,000-pound scale range of machine E, 100,000-pound capacity fluid-support, Bourdon-tube, hydraulic testing machine.*

[Gage throttle valve open one-fourth turn.]

The results of the tests made with the 0- to 50,000-lb scale range, as shown in figure 18, indicate that the error is independent of the load. The error without the maximum pointer is almost directly proportional to the rate of loading. The error with the maximum pointer is in general greater than the error without the maximum pointer for all rates of loading. The tests with this scale range were made with the throttle valve open one-fourth turn, which is within the range of opening of one-eighth to one-fourth turn recommended by the manufacturer.

The results of the tests made with the 0- to 10,000-lb scale range, given in figure 19, show the error for two different openings of the throttle valve, one-fourth turn and one turn. The error is directly proportional to the rate of loading for both throttle valve openings

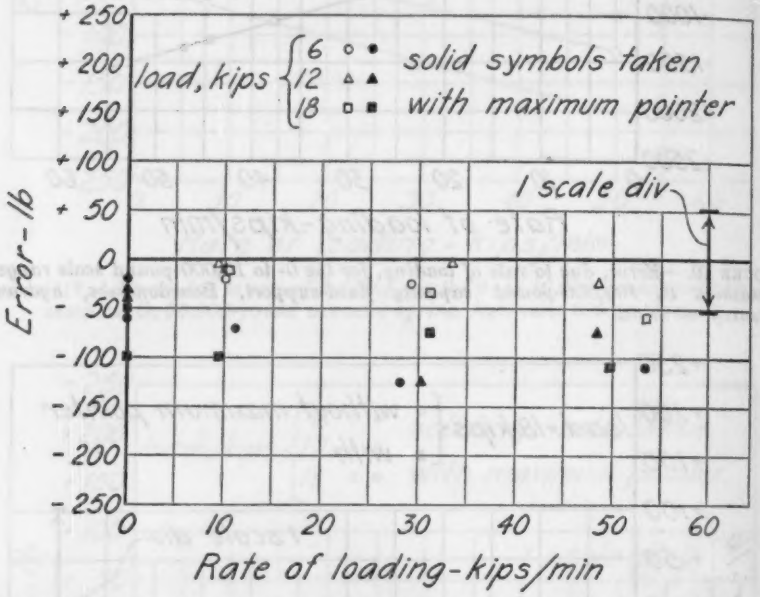

FIGURE 21.—*Error, due to rate of loading, for the 0- to 75,000-pound scale range of machine F, 75,000-pound capacity fluid-support, Bourdon-tube, hydraulic testing machine.*

and in each case the readings taken with the maximum pointer agree closely with the readings taken without the maximum pointer. The error for an opening of one-fourth turn of the throttle valve is about 15 times the error for an opening of one turn for a given rate of loading. This error could probably be reduced by using a less viscous fluid in the weighing system.

The results of the tests made with the 0- to 100,000-lb scale range, given in figure 20, were obtained with the throttle valve open one-fourth turn. The error without the maximum pointer is almost directly proportional to the rate of loading. The error with the maximum pointer is approximately equal to the error without the maximum pointer plus a constant error.

6. MACHINE *F*

The results of the tests made with the 0- to 75,000-lb and 0- to 10,000-lb scale ranges of machine *F* are given in figures 21 and 22. For both scale ranges the errors without the maximum pointers appear to be almost directly proportional to the rate of loading and in each case the error with the maximum pointer is greater than the error without the maximum pointer for all rates of loading. The results of the tests made with the 0- to 75,000-lb scale range, given in figure 21, indicate that the error is independent of the load.

7. EFFECT OF ERROR DUE TO RATE OF LOADING ON LOADING RANGE

The American Society for Testing Materials [6] defines the loading range of a testing machine as the range of indicated loads for which

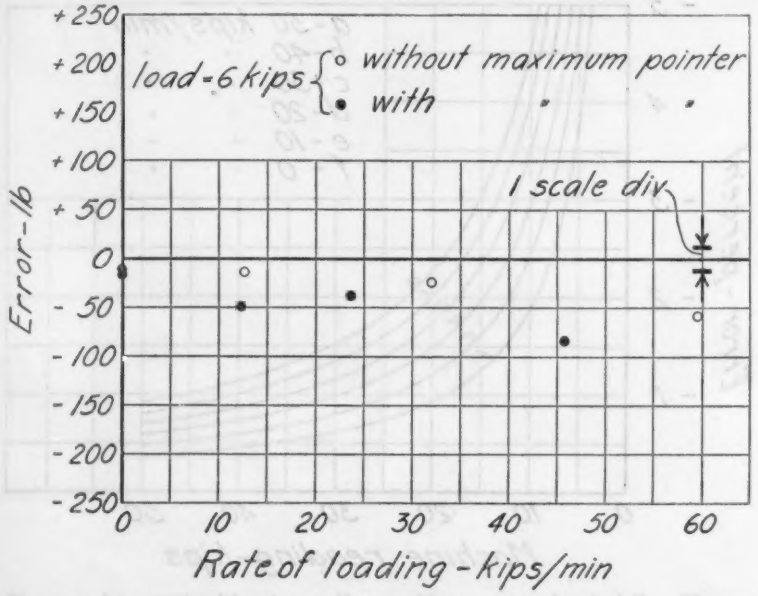

FIGURE 22.—*Error, due to rate of loading, for the 0- to 10,000-pound scale range of machine F, 75,000-pound capacity fluid-support, Bourdon-tube, hydraulic testing machine.*

the testing machine gives results within a tolerance of ±1 percent. The loading ranges of testing machines are usually determined for static loads. The additional errors, due to rate of loading, will, in general, decrease the loading ranges.

The relation between the machine reading, the rate of loading, and the error with the maximum pointer, due to rate of loading, for the 0- to 50,000-lb scale range of machine *D* is shown in figure 23. The curves were computed from values taken from figure 16. It is clear from figure 23 that even if the errors for static loading without the maximum pointer were zero, the loading range would be greatly reduced by the use of the maximum pointer and still further reduced by increasing the rate of loading.

[6] Am. Soc. Testing Materials Standards I, 849–860 (1936).

V. CONCLUSIONS

Six testing machines comprising four different types were calibrated for rates of loading up to approximately 50,000 lb/min by means of a special elastic calibrating device. The error due to rate of loading was determined with and without the maximum pointers for all machines except machine *A*, the beam-and-poise, screw-driven machine. The error due to overrunning the poise of machine *A* was determined.

For each scale range for which the relationship between the error due to rate of loading, determined without the maximum pointer, and the rate of loading could be determined, the error was almost directly proportional to the rate of loading. For all machines showing an effect the indicated load of the machine was less than the applied load.

For the one scale range of each machine tested at different loads the error due to rate of loading was independent of the applied load.

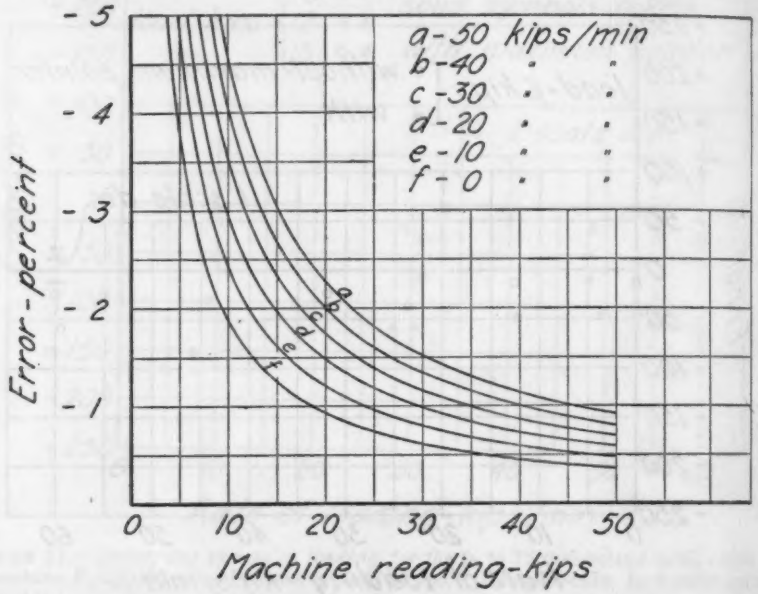

FIGURE 23.—*Relation between machine reading, rate of loading, and error with the maximum pointer for the 0- to 50,000-pound scale range of machine D, 50,000-pound capacity spring, hydraulic testing machine.*

The additional error due to the use of the maximum pointer was in some cases as great as −200 lb, while in other cases it was too small to be measured by the methods used. This error could probably be reduced for some of the scale ranges of some of the machines, but no special adjustments were made to the maximum pointers before or during these tests.

The error caused by overrunning the poise of machine *A* appears to be almost directly proportional to the rate of loading. For this machine only, the indicated load was greater than the applied load.

The additional errors, due to rate of loading, of the testing machines calibrated, at rates of loading currently used in testing, exceeded in several cases the tolerances specified for testing machines. These errors, therefore, cannot in general be neglected when determining the rates of loading to be used in materials testing.

The errors caused by the rate of loading of different testing machines of the same type may differ materially because of small inherent differences in the weighing systems and slight differences of adjustment. For this reason the results of these tests cannot be used to correct the load readings of other testing machines of the same types.

WASHINGTON, April 12, 1937.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1010

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DETERMINATION OF PHOSPHORIC ANHYDRIDE IN PHOSPHATE ROCK, SUPERPHOSPHATE, AND "METAPHOSPHATE"

By James I. Hoffman and G. E. F. Lundell

ABSTRACT

A gravimetric method requiring no molybdate reagent is described for the determination of phosphoric anhydride in phosphate rock and similar materials. In this method a precipitation with a large excess of magnesia mixture in the presence of ammonium citrate serves to separate the phosphate ion from the other constituents. A second precipitation yields a precipitate of definite composition which is converted to magnesium pyrophosphate, $Mg_2P_2O_7$, on ignition. The method has been successfully applied to phosphate rock, superphosphate, "metaphosphate", and liquids used with silicate cements in dentistry. It is recommended for use in standardization and umpire analyses of phosphate rocks and similar materials, but it is not sufficiently rapid to replace the usual volumetric method now employed in routine analyses.

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I. INTRODUCTION

For the accurate determination of phosphorus pentoxide in phosphate rock and similar materials, it has been customary first to precipitate the phosphate ion as yellow ammonium phosphomolybdate in order to separate it from calcium, iron, aluminum, and other constituents.[1] In the usual procedure, the yellow precipitate is dissolved in ammonium hydroxide, magnesia mixture is added, and magnesium ammonium phosphate containing impurities is precipitated. The impure precipitate is dissolved in hydrochloric acid, more magnesia mixture is added, and the phosphorus is precipitated as magnesium ammonium phosphate under closely controlled conditions so that a precipitate of definite composition is obtained. This precipitate is then ignited at 1,050 to 1,100° C, and the residue is weighed as magnesium pyrophosphate, $Mg_2P_2O_7$. Slightly high and somewhat erratic results are usually obtained if only one precipitation with magnesia mixture is made.

[1] See G. E. F. Lundell and J. I. Hoffman, *The analysis of phosphate rock*, J. Assn. Official Agr. Chem. 8, 184 (1924).

In 1924 the authors [2] observed that a relatively large amount of calcium oxide, added to the phosphate solution, did not cause any error in the determination of phosphorus pentoxide if two precipitations with magnesia mixture were made in the presence of ammonium citrate. It was also shown that under the same conditions ammonium citrate prevented the precipitation of iron and aluminum. These observations suggested the possibility of precipitating the phosphorus directly with magnesia mixture in the presence of the calcium, aluminum, iron, and other constituents of the phosphate rock, thus eliminating the usual preliminary precipitation with molybdate reagent. Numerous tests were accordingly made which showed that under proper conditions the phosphorus pentoxide in a solution of phosphate rock and similar materials can be determined by (1) precipitating directly with a large excess of magnesia mixture; (2) filtering; (3) dissolving the precipitate; (4) precipitating with the usual small excess of magnesia mixture; (5) filtering; (6) igniting the precipitate; and (7) weighing the residue as magnesium pyrophosphate. The details of this procedure are given in section II.

II. PROCEDURE

1. PREPARATION OF THE SOLUTION

Method A. (*Applicable to phosphate rock and superphosphate*).—Transfer 2.500 g of the dried material to a 300-ml Erlenmeyer flask, add 30 ml of hydrochloric acid and 10 ml of nitric acid. Place a small watch glass over the mouth of the flask, and boil gently for 30 minutes. Rinse the glass, add 50 ml of water, heat to boiling, and filter through a paper of close texture, catching the filtrate in a 250-ml volumetric flask. Wash the paper [3] and the Erlenmeyer flask thoroughly with diluted hydrochloric acid [4] (1+4), cool the contents of the volumetric flask to the proper temperature, and add water until the flask is filled to the mark. Mix thoroughly and transfer 50.00 ml of the solution (representing 0.5000 g of sample) to a 300-ml Erlenmeyer flask.

Method B (*Applicable to phosphate rock and superphosphate*).—Transfer 0.5000 g of the dried material to a 300-ml Erlenmeyer flask, and add 15 ml of hydrochloric acid and 3 ml of nitric acid. Place a small watch glass over the mouth of the flask, and boil gently for 30 minutes. Rinse and remove the watch glass, and, without filtering, proceed with the addition of ammonium citrate, hydrochloric acid, and magnesia mixture as described in 2.

This method obviates the use of volumetric glassware and requires less time than method *A*. The results obtained are equally accurate if the material contains no appreciable amount of insoluble compounds of phosphorus.

[2] J. Assn. Official Agr. Chem. 8, 188 (1924).

[3] By applying the treatment prescribed, no phosphorus is volatilized, and only 0.03 percent of P_2O_5 remains in the insoluble residue in the case of the National Bureau of Standards Sample 56, and less than 0.005 percent in Samples 56a and 120. Unless it is known that no phosphorus remains insoluble, ignite the paper and insoluble residue in platinum, fuse with a small quantity of sodium carbonate, and leach the cooled melt with hot water. Filter, acidify the filtrate with hydrochloric acid, and add the solution to the contents of the volumetric flask. Or alternatively, if the filtrate is acidified with nitric acid, the phosphorus may be precipitated with molybdate reagent, separately determined, and the percentage found added to that obtained in the main determination.

[4] This denotes 1 volume of concentrated hydrochloric acid (sp gr 1.18) diluted with 4 volumes of water. Diluted ammonium hydroxide (1+19) denotes 1 volume of ammonium hydroxide (sp gr 0.90) diluted with 19 volumes of water. If no dilution is specified, the concentrated reagent is meant. This system of specifying diluted acids is used throughout this paper.

Method C (Applicable to "metaphosphate", superphosphate, and phosphate rock).—Transfer 0.5000 g of the material to a platinum dish, and add 10 ml of water, 5 ml of hydrofluoric acid, and 20 ml of nitric acid. Digest, and evaporate on the steam bath until only about 5 ml of solution remains. Then add 10 ml of water and 20 ml of nitric acid, and again evaporate until only about 5 ml of solution remains. Add 50 ml of diluted nitric acid (1+99), and digest on the steam bath for 10 minutes. Transfer the solution to a 300-ml Erlenmeyer flask, and proceed with the addition of ammonium citrate, hydrochloric acid, and magnesia mixture as described in 2.

2. DETERMINATION OF PHOSPHORIC ANHYDRIDE

To the solution in the 300-ml Erlenmeyer flask, add 30 g of ammonium citrate, 10 ml of hydrochloric acid, and 100 ml of magnesia mixture.[5] Neutralize the solution with ammonium hydroxide, using litmus paper as indicator, and add 3 ml of ammonium hydroxide in excess. Dilute the solution to 225 to 250 ml with water, add a few glass beads, stopper the flask tightly, shake on a shaking machine for about one-half hour, and allow to stand overnight. Filter through a paper of close texture, and wash the flask and paper once with a small quantity of diluted ammonium hydroxide (1+19). Discard the filtrate.

Dissolve any magnesium ammonium phosphate remaining in the flask in about 50 ml of warm diluted hydrochloric acid (1+4), and pour the solution through the paper to dissolve the phosphate that was transferred to the filter, and to separate any insoluble residue that may have remained if method *B* or *C* was used for the preparation of the solution. Wash the paper and flask with more of the same acid, and add 0.3 g of citric acid and 1 ml of magnesia mixture to the solution, which should have a volume of about 100 ml. While stirring, add ammonium hydroxide until the solution is alkaline to litmus, and then add 5 ml in excess. Stir occasionally during one-half hour, and allow to stand for 4 hours or overnight.

Collect the precipitate on a 9-cm paper of close texture, wash with cool diluted ammonium hydroxide (1+19), and transfer the paper and precipitate to a weighed platinum or porcelain crucible. Char the paper without flaming, burn off the carbon below 900° C, and finally ignite to constant weight, preferably in a muffle, at 1,050 to 1,100° C.

The weight of the magnesium pyrophosphate, $Mg_2P_2O_7$, multiplied by 63.79 and divided by the weight of the sample yields the percentage of P_2O_5 in the sample.

Tests have shown that in the analysis of phosphate rock the time of standing in the first precipitation can be reduced to 3 hours and in the second to 2 hours, if the solutions are chilled before shaking or stirring and then allowed to stand in ice water or in a refrigerator at 5 to 10° C. With small quantities (less than 10 mg of P_2O_5), the longer time of standing is essential, and even then it is best to chill and shake alternately two or three times. (See footnote *d* under table 1.)

[5] Prepare the magnesia mixture as follows: Dissolve 400 g of $MgCl_2.6H_2O$ and 300 g of ammonium chloride in 1,500 ml of warm water. When solution is complete, add ammonium hydroxide until the solution is alkaline to litmus. Allow to stand for about 1 hour, filter, and add hydrochloric acid to the filtrate until the solution is acid to litmus. If properly prepared, the volume of the solution is almost exactly 2 liters.

III. RESULTS OBTAINED IN THE USE OF THE METHOD

The results obtained for phosphoric anhydride in synthetic solutions and in solutions of phosphate rocks and similar materials are shown in tables 1 and 2. The solution of phosphoric acid that was used in adding known amounts of phosphorus in preparing the mixtures designated in table 1 was standardized by the method involving two precipitations with magnesia mixture.[6] The "other substances present" in table 1 and the "substances added" in table 2 were tested and found to be free from phosphorus.

TABLE 1.—*Results obtained for P_2O_5 by applying the procedure to solutions of synthetic mixtures*

P_2O_5 present (standard solution of H_3PO_4)	P_2O_5 found	Other substances present
g	g	g
0.0783	[a] 0.0780	0.20 Al_2O_3, 0.20 Fe_2O_3, 0.05 ZnO, 0.3 CaO, 0.03 MnO.
.0822	.0821	.10 Al_2O_3, .20 Fe_2O_3, .3 CaO.
.0880	[b] .0881	.10 Al_2O_3, .20 Fe_2O_3, .3 CaO.
.1068	.1067	.10 Al_2O_3, .20 Fe_2O_3, .3 CaO.
.0107	[c] .0106	.10 Al_2O_3, .20 Fe_2O_3, .3 CaO.
.0031	.0027	.10 Al_2O_3, .20 Fe_2O_3, .3 CaO.
.0031	[d] .0031	.10 Al_2O_3, .20 Fe_2O_3, .3 CaO.

[a] Tests showed that the ignited pyrophosphate contained no significant amounts of ZnO and MnO.
[b] A test showed that the ignited pyrophosphate contained approximately 0.1 mg of Fe_2O_3.
[c] A test showed that the ignited pyrophosphate contained less than 0.1 mg of CaO.
[d] To obtain this result, the solution was chilled at the beginning of the first precipitation, shaken for 1 hour, allowed to stand at 5 to 10° C overnight, shaken again for 1 hour, and then allowed to stand 2 or 3 hours before filtering. The ignited pyrophosphate contained no Al_2O_3, no CaO, and less than 0.1 mg of Fe_2O_3.

[6] See J. I. Hoffman and G. E. F. Lundell, BS J. Research 5, 279 (1930) RP200.

TABLE 2.—*Results obtained for P_2O_5 by applying various methods to phosphate rocks, superphosphate, and other materials*

Material (0.5-g samples)	Substances added	Double precipitation with magnesia mixture without preliminary molybdate precipitation. Method described in text. Solution for analysis prepared by—			Molybdate precipitation followed by two precipitations with magnesia mixture. J. Assn. Official Agr. Chem. 8, 194 (1924)	Molybdate precipitation followed by one precipitation with magnesia mixture. (Official method of AOAC 1935)
		Method *A*	Method *B*	Method *C*		
	g	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Standard sample NBS 56		31.32	[a] 31.28		31.32	31.56
Do			[a] 31.35		31.35	31.34
Do					31.31	31.36
Do					31.34	31.39
Do	1.8 H_2SO_4	31.30				
Do	.20 Al_2O_3	[b] 31.33				
Do	.005 ZrO_2	[c] 31.28				
Do				31.35		
Standard sample NBS 56a		32.87	[a] 32.88		32.92	32.89
Do			[a] 32.90		32.90	33.03
Do					32.86	
Do					32.89	
Do	.40 Fe_2O_3	[d] 32.92				
Do	1.0 H_2SO_4	32.89				
Standard sample NBS 120		35.13	[a] 35.17		35.19	35.28
Do		35.17			35.13	35.47
Do					35.18	
Do					35.19	
Do	.02 TiO_2, .03 F	[e] 35.17				
Do	.1 Al_2O_3, .2 Fe_2O_3, .05 ZnO, .06 MnO	[f] 35.19				
Do				35.16		
TVA "treble" superphosphate [g]		49.55	49.60	49.60	49.55	[h] 49.68
TVA "metaphosphate" [g]			[i] 64.65	64.52, 64.60	64.50	
Cement liquid [j]		44.93, 44.91			44.96, 44.90	

[a] Tests showed that the ignited pyrophosphates contained no significant amounts of CaO or SiO_2. The certificate value for P_2O_5 in this sample is 31.32 percent.

[b] The ignited pyrophosphate was examined for Al_2O_3. No significant amount was found.

[c] After dissolving the first precipitate of magnesium ammonium phosphate by pouring dilute hydrochloric acid through the filter, the paper was ignited at a low temperature and the residue examined for ZrO_2 and P_2O_5. A little ZrO_2 and about 0.2 mg of P_2O_5 were found.

[d] The ignited pyrophosphate contained about 0.2 mg of Fe_2O_3.

[e] No titanium was found in the ignited pyrophosphate.

[f] Tests showed that the ignited pyrophosphate contained no significant amounts of ZnO and MnO.

[g] The samples of these materials were furnished through the courtesy of W. H. MacIntire, chemist, Tennessee Valley Authority, Knoxville, Tenn. These superphosphates and "metaphosphates" are similar to phosphate rocks in composition, excepting that the percentage of P_2O_5 is greater. For a discussion of the "metaphosphate" see W. H. MacIntire, L. J. Hardin, and F. D. Oldham, Ind. Eng. Chem. **29**, 234 (1937).

[h] Result obtained volumetrically 2 years ago by W. H. MacIntire.

[i] The condition of the silica in this material is such that filtration is very slow. Consequently method *C* for the preparation of the solution is recommended.

[j] Analysis by I. C. Schoonover. These liquids, used with silicate cements in dentistry, also contain zinc and in some cases aluminum and magnesium. The zinc is now regularly determined in the filtrate obtained from the precipitation with magnesia mixture.

IV. DISCUSSION OF THE METHOD AND ITS APPLICATION

An inspection of the data shows that very accurate results can be obtained for phosphoric anhydride without the preliminary precipitation with molybdate reagent. During the precipitations with magnesia mixture, the solutions must stand for considerable periods, but not much of the analyst's time is required. Iron, aluminum, titanium, silica, calcium, zinc, manganese, fluorine, and organic matter in the percentages found in phosphate rock [7] do not interfere.

[7] For the composition of phosphate rock, see K. D. Jacob, W. L. Hill, H. L. Marshall, and D. S. Reynolds, Tech. Bul. 364, U. S. Department of Agriculture, Washington, D. C. (1933).

Sulphates and nitrates, which might be introduced in the manufacture and mixing of fertilizers, likewise do not interfere. Under the conditions set forth in the procedure, only part of the arsenic in the original material appears in the ignited pyrophosphate. This is of no consequence, since 0.014 is the highest percentage that has been reported in the extensive survey made by Jacob and his coworkers. If much arsenic should be encountered, it can easily be removed from the material by a preliminary separation by means of hydrogen sulphide.

There is some doubt concerning the complete precipitation of pyrophosphates and metaphosphates by means of magnesia mixture.[8] The TVA "metaphosphate" (no. 23 in table 2) contains phosphorus in a form other than orthophosphate. For example, if the material is treated with cold diluted nitric acid (1+4), and molybdate reagent is added to the resulting solution, part of the phosphorus remains unprecipitated for as much as 48 hours. If, however, the nitric acid solution is gently boiled for 30 minutes before the molybdate reagent is added, precipitation is complete in the normal short time (30 to 60 minutes) that is required for orthophosphates. This boiling with diluted nitric acid (1+4) is prescribed by W. H. MacIntire[9] for the conversion of metaphosphate to orthophosphate. Tests showed that solutions of the "metaphosphate" prepared by methods *B* and *C* react toward molybdate reagent and toward magnesia mixture exactly like those prepared by boiling for 30 minutes with diluted nitric acid (1+4). Two hours of additional boiling with diluted nitric acid (1+4) did not cause any significant change in the amount of phosphoric anhydride found in this material. Since the additional boiling did not cause the results to be higher, and since MacIntire's work indicates that complete conversion is effected by boiling for 30 minutes, the treatments given in methods *B* and *C* were regarded as satisfactory for complete conversion to the orthophosphate. Method *C* was found preferable in the case of the metaphosphate because the use of hydrofluoric acid eliminates the gelatinous silica which would otherwise render filtration very slow.

The use of 30 g of ammonium citrate is recommended in the procedure. A much smaller quantity will easily prevent the precipitation of iron and aluminum in a solution of a 0.5-g sample of material containing as high as 40 percent of iron oxide or alumina. It was found, however, that these large amounts of iron or aluminum, even though they remain in solution, prevent the complete precipitation of phosphorus by magnesia mixture unless a large excess of ammonium citrate is present.

The method is applicable to phosphate rock, superphosphate, "metaphosphate", and similar materials. Its application in the analysis of liquids used with silicate cements in dentistry has also been demonstrated. (See table 2.)

For routine analyses it is not sufficiently rapid, however, to replace the much used volumetric method in which the ammonium phosphomolybdate is dissolved in a standard solution of sodium hydroxide.

WASHINGTON, May 21, 1937.

[8] Th. Wilhelm Fresenius, *Introduction to Qualitative Chemical Analysis*, translated by C. Ainsworth Mitchell, p. 418, 1921 ed., J. Wiley and Sons, New York, N. Y.

[9] Private communication.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1011

Part of Journal of Research of the National Bureau of Standards, Volume 19, July 1937

SUBSTITUTION OF DOMESTIC FOR IMPORTED CLAYS IN WHITEWARE BODIES

By William W. Meyer and Theron A. Klinefelter

ABSTRACT

Domestic kaolins and ball clays were substituted for imported clays in whiteware bodies of the more important types. The substitutions were based on compositions in terms of RO, RO_2, and R_2O_3, of the bodies and raw materials, and on physical properties of the raw materials and those required of the bodies. Laboratory tests of dried and heat-treated specimens indicated that the properties of imported-clay bodies could be duplicated by domestic-clay bodies and factory tests showed that in most cases this would involve only minor changes in plant procedure. The vitrification temperatures of whiteware bodies were correlated with their RO contents. The plasticities and the strengths of the dry specimens depended chiefly on the ball clay contents of the bodies. The RO and ball clay contents can be varied widely with little effect on the physical properties of whiteware bodies heated to the same degree of vitrification.

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I. INTRODUCTION

Numerous investigations of whiteware bodies have proved that the preparation and properties of each raw material employed, as well as the method of preparing the body and forming the ware, all have their effects upon the properties of the product. These factors should be borne in mind whenever one raw material is substituted for another.

In previous attempts to substitute domestic for imported clays the experimental work was largely of an empirical nature. The cost entailed by such procedure was so great that investigations have since been made by various workers to obtain fundamental data which would make possible such substitutions by scientific methods.

The present paper follows reports of two investigations dealing with china clays and kaolins.[1] The first [2] covered the essential

[1] In this paper the choice of the terms "kaolin" and "china clay" is based on commonly accepted usage.
[2] J. Am. Ceram. Soc. 16, 209 (1933).

properties of English china clays since they constituted the largest volume of imported clays. The second [3] report dealt with representative American kaolins. It suggested a method of modifying the kaolins to make them simulate the properties of the china clays by adding such materials as were necessary to bring the mixtures containing the domestic clays to the same fluxing content as that of the imported clays. That investigation showed that a mere substitution of a kaolin or a combination of kaolins for china clay would be apt to change considerably many of the body's properties.

The present investigation aims to establish a less empirical method of arriving at body formulas by specifying not only the clay content but also, to a certain extent, the chemical formulas.

The method of attacking the problem of substitutions is presented in this report with supporting data obtained by attempting to duplicate the commercial bodies containing imported clays, in whole or in part, with bodies prepared from domestic materials.

II. MATERIALS AND METHODS

Three kaolins were chosen for this work as representative of their types. The imported china clay and ball clay and the American ball clays, feldspars, and flint were materials on hand, the chemical compositions of which were known. The chemical compositions of these materials and their compositions in terms of RO, RO_2, and R_2O_3, which serve as the basis for batch calculations, are given in table 1.

TABLE 1.—*Compositions of raw materials*

Material	Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	RO	RO_2	R_2O_3
	%	%	%	%	%	%	%	%	%	%	%	%
English ball clay	15.1	46.4	35.5	0.8	0.8	0.2	0.4	1.0	0.1	1.7	47.2	36.3
English china clay	12.4	47.0	37.7	.9	.2	.2	.2	1.6	.2	2.2	47.2	38.6
Kentucky ball clay 4	14.7	49.9	31.4	.6	1.5	.2	.3	1.2	.2	1.9	51.4	32.0
Tennessee ball clay 5	13.6	50.3	31.5	.6	1.3	.2	.3	2.0	.3	2.8	51.6	32.1
Florida (ball) kaolin	13.7	46.3	37.7	.8	.5	.5	(a)	0.2	.0	0.7	46.8	38.5
Georgia kaolin	13.7	45.7	38.7	.3	1.4	.2	(a)	.0	(a)	.2	47.1	39.0
North Carolina kaolin	13.2	47.9	37.4	.4	.0	.1	(a)	1.0	.1	1.2	47.9	37.8
Maine feldspar	0.3	72.7	15.1	.1	.1	.3	(a)	8.3	3.1	11.7	72.8	15.2
Buckingham feldspar	.3	66.5	18.2	.1	.0	.2	.1	12.4	2.0	14.7	66.5	18.3
Flint	------	100	------	------	------	------	------	------	------	------	100	------

[a] Trace.

Having chosen the approximate percentages of certain of the raw materials in the body [4] and knowing the compositions of the raw materials and of the heated body being formulated, the calculation of the batch formula becomes comparatively simple. In the simulation of a body it is possible to use as a starting point either the chemical composition of the heated body or the batch formula. Both of these were tried in this study. As a simplification most of the bodies were formulated by using only one kaolin or china clay, one feldspar, and no auxiliary flux.

[3] J. Am. Ceram. Soc. 18, 163 (1935).

[4] Certain assumptions must be made. The ball clay content must be assumed, for experience has shown that batch formulas calculated from chemical compositions will not necessarily give satisfactory results unless various physical properties are taken into consideration. It is also necessary to decide if more than 1 kaolin or more than 1 feldspar is to be used and, if so, the approximate proportions of the two like materials.

Method of calculation.—By chemical analysis of a sample of heated electrical porcelain it is found that its percentage composition can be expressed as:

$$RO = 5.30$$
$$RO_2 = 70.70$$
$$R_2O_3 = 24.00$$

A body of this type requires a ball clay content of approximately 25 percent to give it the desired properties prior to heat treatment, and the use of more than one type of ball clay is desirable. With the above information and the RO, RO_2, and R_2O_3 contents of the raw materials known (table 1), the percentage of each raw material in the batch formula is calculated as follows:

Heated body *L5*			Raw materials		
RO	RO_2	R_2O_3	Parts[a]		Percent[d]
%	%	%			
5.30	70.70	24.00			
0.24	6.43	4.00	[b]0.125	Kentucky ball clay	11.67
5.06	64.27	20.00			
0.35	6.45	4.01	.125	Tennessee ball clay	11.67
4.71	57.82	15.99			
4.66	28.97	6.05	[c].398	Maine feldspar	37.16
0.05	28.85	9.94			
0.05	12.01	9.94	[c].255	Georgian kaolin	23.81
0.00	16.84	0.00			
	16.80		.168	Flint	15.69
	0.04		1.071		100.00

[a] Total exceeds 1.000 because the analyzed body had been heated, while raw materials contain water, organic matter, etc.

[b] 0.125 represents one-half of the empirically chosen ball clay content and multiplied by the RO, RO_2, and R_2O_3 contents, respectively, of Kentucky ball clay, table 1, yields 0.24 percent of RO, 6.43 percent of RO_2, and 4.00 percent of R_2O_3.

[c] Arrived at as follows: Since the feldspar and kaolin must furnish the remainder of RO and R_2O_3, let x=parts of feldspar required and y=parts of Georgia kaolin required.

Then:

$11.7x + 0.2y = 4.71$ (the feldspar contains 11.7 percent of RO and the kaolin 0.2 percent.)

$15.2x + 39.0y = 15.99$ (the feldspar contains 15.2 percent of R_2O_3 and the kaolin 39.0 percent.)

Solving, $x = 0.398$ part feldspar.

$y = 0.255$ part kaolin.

[d] Parts/1.071×100=percent.

All bodies were made in slip form, using about 30 percent of water, with sodium silicate as the deflocculant, and cast in plaster molds. The test specimens were about 7 by 1 by 1 cm.

Test specimens were heated in an electric furnace, the schedule being 6 hours to reach the desired temperature, which was held 1 hour, after which the furnace was allowed to cool overnight. Accuracy of temperature control was found to be important. A difference of as little as 5 to 10° C in maximum temperature of the heat treatment resulted in a measurable difference in the properties of some bodies, especially in the case of apparent porosity. The temperature of heat treatment

desired was, in most cases, the minimum required for vitrification and, as a result, most of the specimens had not attained maximum bulk specific gravity. The properties of the test specimens were determined by standard methods.

III. LABORATORY TESTS

In the preliminary work kaolin was substituted for china clay in vitreous and semivitreous tableware, electrical porcelain, and sanitary ware. Batch formulas were based on bodies recommended to the Bureau by the industry at one time or another. Using the data in table 1, chemical formulas (formulas in terms of RO–RO_2–R_2O_3 percentages) of the reference bodies, and batch formulas of the bodies containing substitutions, were calculated. These batch and chemical formulas are given in table 2. Body *V9* differs from *V8* only in the brand of feldspar used and the flint content. The proportions of North Carolina and Florida kaolins used in substituting a mixture of these two clays for china clay are based on their exchange capacities, shrinkages, particle sizes, and strengths.

Data collected are given in table 2.

It was difficult to distinguish the china clay bodies from the kaolin bodies in appearance when both received the minimum heat treatment productive of maximum bulk specific gravity. In the semivitreous condition the presence of appreciable amounts of TiO_2 in the Georgia and South Carolina kaolins caused a cream-white color.

Following these preliminary tests, samples of commercial bodies were solicited from a number of whiteware producers. Of the samples received, two electrical porcelains, two sanitary-ware bodies, one vitreous-china body, one wall-tile body, and one vitreous floor-tile body were analyzed and their compositions calculated in terms of RO, RO_2, and R_2O_3. The RO, RO_2, and R_2O_3 contents of the feldspars used by the producers were also calculated from chemical compositions furnished by them. These data and the reported heat treatments used in the plants, together with the bulk specific gravities and apparent porosities of the heated specimens, determined on the samples furnished the laboratory, are presented in table 3. Samples *P1*, *P5*, and *P6* were formed by casting, samples *P2* and *P8* by dry-pressing, and samples *P3*, *P4*, and *P7* by plastic processing. The following information was furnished by the producers: The floor- and wall-tile bodies (*P8* and *P2*) and the semivitreous-china body (*P7*) contained all domestic clays; the china clay in one insulator body (*P5*) and both the ball and china clays in the other (*P3*) had been imported; and the clay used in the vitreous-china and the two sanitary-ware bodies (*P4*, *P1*, and *P6*) was nearly all imported.

TABLE 2.—*Preliminary bodies involving substitution of American for English clays in whiteware bodies*

Body	English (Devon) ball clay	English china clay	Tennessee 5 ball clay	Florida (ball) kaolin	North Carolina kaolin	Georgia kaolin	Maine feldspar	Flint	Bulk sp gr of dried bars	Transverse strength of dried bars	Heated 1 hr at	RO	RO_2	R_2O_3	Bulk sp gr of heated bars	Transverse strength of heated bars	Volume shrinkage during heating	Apparent porosity
	%	%	%	%	%	%	%	%		lb/in.²	°C	%	%	%		lb/in.²	%	%
SV1	13.0	24.5		6.0	9.0		12.5	35.0	1.79		1,265	2.5	74.3	23.2	2.23	6,300	25.6	7.2
SV1	13.0	24.5		6.0	9.0		12.5	35.0	1.79		1,225	2.5	74.3	23.2	2.13		22.2	11.5
SV4	13.0			13.5	24.5		15.5	33.5	1.77		1,225	2.5	74.3	23.2	2.04	4,800	19.7	16.1
SV5	13.0			6.0	9.0	22.0	17.0	33.0	1.88		1,225	2.5	74.3	23.2	2.14	5,500	18.4	11.6
HT1	25.0	20.0					32.0	23.0	1.93		1,245	4.9	73.0	22.1	2.34	6,900	23.1	7.5
HT4	25.0			6.0	12.5		34.0	22.5	1.90		1,245	4.9	73.0	22.1	2.30	6,200	23.3	2.6
HT5	25.0					18.0	35.5	21.5	1.93		1,245	4.9	73.0	22.1	2.32	6,200	22.3	1.3
S1	17.5	32.5					25.0	25.0	1.89	350	1,260	4.2	72.4	23.4	2.36	7,100	25.5	2.2
S4	17.5			10.0	20.5		28.5	23.5	1.83	385	1,260	4.2	72.4	23.4	2.28	6,400	25.4	3.4
S5	17.5					29.0	31.0	22.5	1.92	400	1,260	4.2	72.4	23.4	2.34	6,900	23.4	2.4
S8			12.0	8.0	8.0	18.5	30.0	23.5	1.85	305	1,260	4.2	73.0	22.8	2.36	6,600	25.7	2.2
V1	8.0	33.0		6.0			19.0	34.0	1.85	290	1,285	3.3	75.2	21.5	2.31	6,200	25.4	.9
V5	8.0			16.5	20.5		22.5	32.5	1.81		1,295	3.3	75.2	21.5	2.26	6,500	25.1	1.2
V6	8.0			6.0		29.5	25.0	31.5	1.89		1,285	3.3	75.2	21.5	2.32	6,700	23.5	2.4
V7			10.0	5.0		31.0	24.0	30.0	1.87		1,290	3.3	74.7	22.0	2.33	6,990	24.9	1.2
V8			8.0	8.0	8.0	24.5	23.5	28.0	1.85	320	1,290	3.3	73.7	23.0	2.32	7,000	25.5	2.0
V9			8.0	8.0	8.0	24.5	(a)	33.3	1.85	325	1,290	3.3	73.7	23.0	2.31	7,100	25.5	1.4

(a) 18.2 percent of Buckingham feldspar.

TABLE 3.—*Commercial whiteware bodies*

Body [a]	Type of ware	Plant heat treatment	Bulk sp gr of heated pieces	Apparent porosity	Body composition [b]			Feldspar composition			
					RO	RO_2	R_2O_3	RO	RO_2	R_2O_3	K/Na
				%	%	%	%	%	%	%	
P1	Sanitary	Cone 10	2.38	0.3	4.6	70.4	25.0	14.6	65.7	19.5	3.5
P2	Wall tile	Cone 8 to 9	1.92	24.1	2.2	74.3	23.5	12.7	69.3	17.6	2.5
P3	Electrical porcelain.	Cone 10	2.41	0.0	6.3	69.7	24.0	15.0	65.8	18.6	6.2
P4	Vitreous china	1,235° C	2.38	.0	4.9	73.1	22.0	14.9	65.8	19.2	4.1
P5	Electrical porcelain.	Cone 10	2.39	.1	5.3	70.7	24.0	13.4	68.3	17.9	2.3
P6	Sanitary	Cone 11	2.35	1.0	4.8	72.2	23.0	13.8	68.5	17.4	3.6
P7	Semivitreous	Cone 8 (?)	2.07	16.5	2.7	76.7	20.6	13.8	68.2	17.8	5.3
P8	Floor tile	Cone 11 to 12	2.37	0.0	8.1	67.1	24.8	12.5	69.2	17.9	2.1

[a] The digits indicate bodies of corresponding chemical formulas (in terms of percentage RO, RO_2, and R_2O_3) and numbers in table 4.
[b] Calculated from chemical analyses.

From the body compositions (table 3) and the chemical formulas of the raw materials (table 1) body formulas were calculated, using equal parts of Kentucky and Tennessee ball clays, a combination of kaolins found to give satisfactory results in the preliminary work, Maine feldspar and Pennsylvania flint. The RO content of *L8* (table 4) was so great that it was necessary to substitute some of the purer Buckingham feldspar for that from Maine in this body. The temperature of heat treatment was derived in some cases from an approximate correlation between RO content and vitrification temperature of whiteware mixtures already studied and, in others, from data furnished by the manufacturers. In this paper vitrification is defined as that condition obtained by the minimum temperature or heat treatment producing maximum bulk specific gravity. This criterion was used because it was found in preliminary work that some specimens reach maximum bulk specific gravity before minimum apparent porosity and that, after passing the former point, their physical properties were affected adversely.

All of the test bodies (table 4) cast well and after heat treatment appeared to be quite satisfactory. Some specimens of bodies *L3* and *L5* were heated to semivitrification and some to vitrification.

TABLE 4.—*Laboratory bodies simulating commercial bodies*

Body [a]	Kentucky 4 ball clay	Tennessee 5 ball clay	Florida (ball) kaolin	North Carolina kaolin	Georgia kaolin	Maine feldspar	Flint	Total clay	Bulk sp gr of dried bars	Transverse strength of dried bars	Heated 1 hr at	RO	RO_2	R_2O_3	Bulk sp gr of heated bars	Transverse strength of heated bars	Volume shrinkage during heating	Apparent porosity
	%	%	%	%	%	%	%	%		lb/in.²	°C	%	%	%		lb/in.²	%	%
L1	7.0	7.0	4.7	4.7	26.3	32.6	17.7	49.7	1.89	455	1,255	4.6	70.4	25.0	2.37	8,300	25.5	0.3
L2	9.3	9.3	------	------	35.4	13.1	32.9	54.0	1.89	410	1,235	2.2	73.3	23.5	2.16	6,300	19.0	12.0
L3	11.7	11.7	------	------	20.7	45.4	10.5	44.1	1.90	505	1,105	6.3	69.7	24.0	2.30	6,000	22.1	3.0
L3	11.7	11.7	------	------	20.7	45.4	10.5	44.1	1.90	505	1,235	6.3	69.7	24.0	2.38	9,200	24.6	.0
L4	4.7	4.7	4.7	------	22.1	36.3	22.8	40.9	1.90	340	1,245	4.9	73.1	22.0	2.38	6,800	24.7	.4
L5	11.7	11.7	------	------	23.8	37.2	15.6	47.2	1.90	415	1,165	5.3	70.7	24.0	2.25	5,400	20.7	6.4
L5	11.7	11.7	------	------	23.8	37.2	15.6	47.2	1.90	415	1,245	5.3	70.7	24.0	2.38	8,700	24.9	.0
L6	7.0	7.0	4.7	4.7	21.1	34.5	21.0	44.5	1.89	325	1,255	4.8	72.2	23.0	2.39	8,000	25.4	.1
L7	7.0	7.0	4.7	4.7	21.4	17.7	37.5	44.8	1.89	325	1,210	2.7	70.7	20.6	2.14	5,200	16.7	13.0
L8	7.1	7.1	------	------	24.3	[b]59.1	------	38.5	1.89	305	1,230	8.1	67.1	24.8	2.39	8,800	24.9	1.0

[a] The digits denote the chemical formulas to be those of correspondingly numbered bodies in table 3.
[b] And in addition 2.4 percent of Buckingham feldspar.

The composition in terms of RO, RO_2, and R_2O_3 of each body tested is plotted on the triaxial diagram in figure 1. The *M* series of bodies (table 5) located along the straight line *xy* in this diagram was tested in order to establish more closely the relation between RO content and vitrification temperature. These bodies were resorted to in an attempt to minimize the effect of variations in clay, RO_2 and R_2O_3 contents. The line was drawn so that the clay contents of the bodies would be approximately 45 percent, which was about the average of those of the commercial samples, as calculated from the chemical

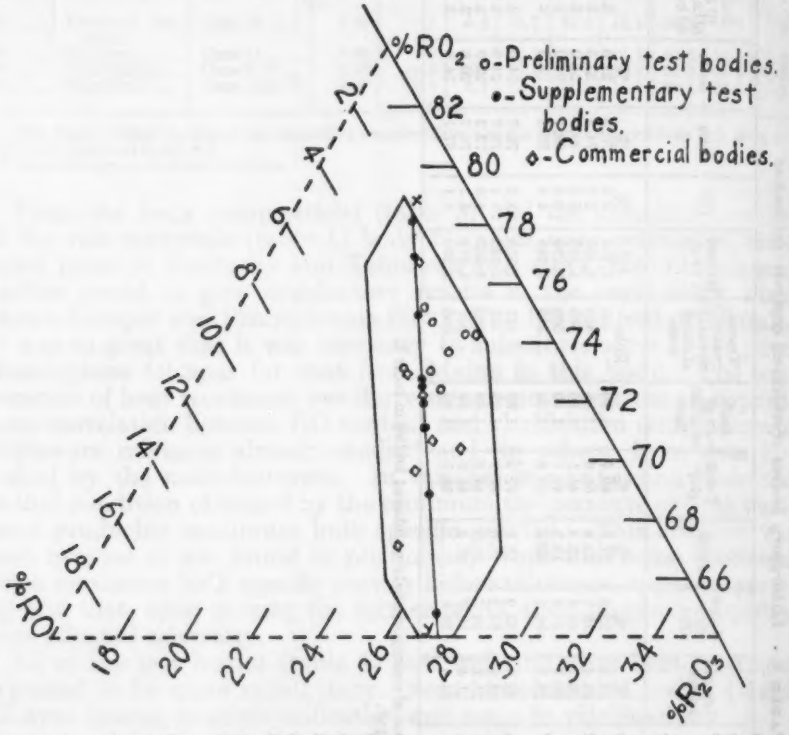

FIGURE 1.—*A portion of the* RO–RO_2–R_2O_3 *system showing the location of the body compositions studied.*

formulas. This clay content is high enough to assure sufficient plasticity, strength, and vitrification range, and also low enough to avoid excessive shrinkage and poor glaze fit. The RO contents of the bodies in the *M* series were the same as those of the commercial bodies (table 3). No attempt was made to vitrify the wall-tile body, but the normally semivitreous-china body was heated to vitrification, and body *M9* was added to fill the gap between 2.7 and 4.6 percent of RO. The relation between temperature of heat treatment and RO content is

shown by the curve in figure 2. This curve is described by the equations:

$T=1398-30R$, from $R=2.5$ to 4.8, and

$$T=\frac{R-6.5}{0.3-0.08R}+1234, \text{ from } R=4.8 \text{ to } 8.5,$$

where:

T=temperature (°C) to which the specimen was subjected for 1 hour

R=the percentage of RO in the ignited body.

Additional data on these bodies are given in table 5. Bodies *M6* and *M7* are identical with *L6* and *L7*, respectively, table 4. Included in table 5 are data on bodies *M2*, *M3*, *M5*, and *M7* heated to less than their vitrification temperatures and bodies *MG*, *EC*, and *MM*, which

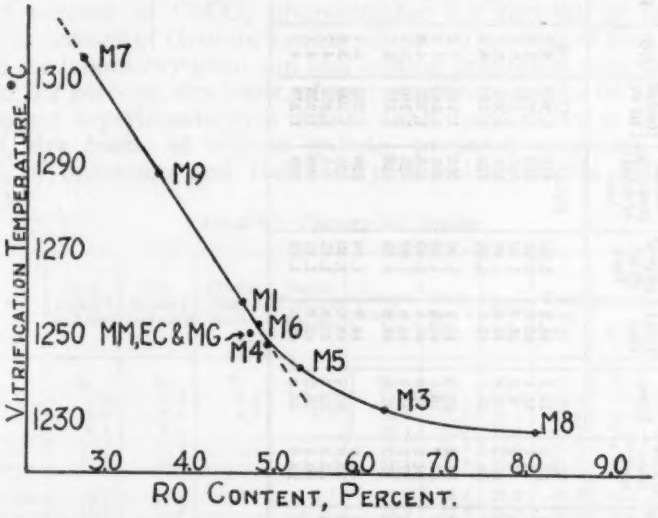

FIGURE 2.—*Relation between minimum vitrification temperature and* RO *content of the bodies studied when heated according to the schedule described on page 67.*

were tested to determine the comparative effects, especially on vitrification temperature, of incorporating magnesium carbonate,[5] china clay, and muscovite mica, respectively. The comparatively low bulk specific gravity of the dry specimens and the great shrinkages during heat treatment of these bodies were caused by accidental addition of excess deflocculant to the casting slips.

[5] The addition of dry magnesium carbonate directly to the body mixture was tried during the preliminary work of this investigation, but the bodies developed tiny blisters. In the present test the salt was mixed with the water before addition of the raw materials, with consequent elimination of the blistering.

TABLE 5.—*Bodies used to determine relation between* RO *content and vitrification temperature*

Body	Kentucky 4 ball clay	Tennessee 5 ball clay	Florida (ball) kaolin	North Carolina kaolin	Georgia kaolin	Maine feldspar	Flint	Total clay	Bulk sp gr of dried bars	Transverse strength of dried bars	Heated 1 hr at	RO	RO_2	R_2O_3	Bulk sp gr of heated bars	Transverse strength of heated bars	Volume shrinkage during heating	Apparent porosity
	%	%	%	%	%	%	%	%		lb/in.²	°C	%	%	%		lb/in.²	%	%
M1	7.0	7.0	4.7	4.7	21.2	32.9	22.5	44.6	1.90	455	1,260	4.6	72.6	22.8	2.39	8,400	25.3	0.1
M2	9.4	9.4	-------	-------	26.7	13.4	41.1	45.5	1.90	370	1,235	2.2	78.1	19.7	2.18	5,900	17.8	10.2
M3	11.7	11.7	-------	-------	22.8	45.2	8.6	46.2	1.90	505	1,165	6.3	68.8	24.9	2.31	6,100	22.6	3.0
M3	11.7	11.7	-------	-------	22.8	45.2	8.6	46.2	1.90	505	1,235	6.3	68.8	24.9	2.39	8,700	25.2	0.0
M4	4.7	4.7	4.7	4.7	24.7	36.2	20.3	43.5	1.89	430	1,250	4.9	72.0	23.1	2.39	7,100	25.5	.0
M5	11.7	11.7	-------	-------	22.9	37.2	16.5	46.3	1.90	505	1,165	5.3	71.1	23.6	2.25	5,700	20.7	6.3
M5	11.7	11.7	-------	-------	22.9	37.2	16.5	46.3	1.90	505	1,245	5.3	71.1	23.6	2.38	9,100	24.9	0.0
M6	7.0	7.0	4.7	4.7	21.1	34.5	21.0	44.5	1.89	325	1,255	4.8	72.2	23.0	2.39	8,000	25.4	.1
M7	7.0	7.0	4.7	4.7	21.4	17.7	37.5	44.8	1.89	325	1,210	2.7	76.9	20.4	2.14	5,200	16.8	12.6
M7	7.0	7.0	4.7	4.7	21.4	17.7	37.5	44.8	1.89	325	1,317	2.7	76.9	20.4	2.38	7,800	25.2	0.3
M8	7.0	7.0	-------	-------	30.0	[a] 34.0	-------	44.0	1.88	320	1,230	8.1	64.8	27.1	2.40	8,700	26.6	.0
M9	7.0	7.0	4.7	4.7	21.2	25.0	30.4	44.6	1.89	325	1,290	3.6	74.9	21.5	2.39	7,600	25.5	.2
MG [b]	4.7	4.7	4.7	4.7	25.0	33.8	22.2	43.8	1.83	315	1,253	4.7	72.4	22.9	2.40	9,500	28.7	.1
EC [c]	4.7	4.7	4.7	4.7	-------	30.1	24.3	45.6	1.83	305	1,253	4.7	72.4	22.9	2.41	9,400	28.7	.1
MM [d]	4.7	4.7	4.7	4.7	22.6	29.9	24.0	41.4	1.83	330	1,253	4.7	72.4	22.9	2.39	9,200	27.9	.1

[a] And in addition 22.0 percent of Buckingham feldspar.
[b] Contains 0.2 percent of $MgCO_3$.
[c] Contains 26.8 percent of English china clay.
[d] Contains 4.7 percent of muscovite mica.

IV. FACTORY TESTS

After making the foregoing tests in the laboratory, body formulas were calculated from the data in tables 1, 3, and 5 and sent to the cooperating manufacturers for testing under commercial conditions. The batch and chemical formulas of these bodies are given in table 6. The following notes were appended to the formulas furnished the manufacturers in case they wished to make minor changes in the ball clay or flux content:

1. 4.7 percent of Kentucky ball clay approximates 5.0 percent of Tennessee ball clay, minus 0.3 percent of feldspar.
2. 1.0 percent of Tennessee ball clay approximates 0.78 percent of Georgia kaolin, plus 0.16 percent of feldspar, plus 0.06 percent of flint.
3. 4.7 percent of North Carolina kaolin approximates 4.7 percent of Georgia kaolin, plus 0.3 percent of feldspar.
4. 1.0 percent of $CaCO_3$ approximates 3.8 percent of feldspar, minus 1.9 percent of Georgia kaolin, minus 1.6 percent of flint.
5. In the laboratory good slip and casting properties were obtained by using 0.2 percent, dry basis, of sodium silicate as the deflocculant. (Subsequent experiments with deflocculants have shown 0.12 to 0.13 percent, dry basis, of sodium gallate, prepared according to the formula of Schramm and Hall [6] to give better results with these bodies.)

TABLE 6.—*Factory test bodies*

Body [a]	Kentucky 4 ball clay	Tennessee 5 ball clay	Florida (ball) kaolin	North Carolina kaolin	Georgia kaolin	Feldspar [b]	Flint	Total clay	Ignited basis		
									RO	RO_2	R_2O_3
	%	%	%	%	%	%	%	%	%	%	%
T11	7.0	7.0	4.7	4.7	20.0	26.1	24.5	49.4	4.6	70.4	25.0
TM61	7.0	7.0	4.7	4.7	20.8	27.7	28.1	44.2	4.8	72.2	23.0
TM22	9.4	9.4			26.4	12.3	42.5	45.2	2.2	78.1	19.7
T33	11.7	11.7			21.5	35.3	19.8	44.9	6.3	69.7	24.0
TM63	11.7	11.7			23.5	29.0	24.1	46.9	5.3	71.1	23.6
TM44	4.7	4.7	4.7	4.7	24.8	28.5	27.9	43.6	4.9	72.0	23.1
TM55	11.7	11.7			22.5	32.6	21.5	45.9	5.3	71.1	23.6
TM66	7.0	7.0	4.7	4.7	21.5	29.2	25.9	44.9	4.8	72.2	23.0
TM77	7.0	7.0	4.7	4.7	21.4	15.0	40.2	44.8	2.7	76.9	20.4
TM88	7.1	7.1			27.1	57.9	0.8	41.3	8.1	64.8	27.1

[a] *T* denotes test body; *M* indicates that the composition, as in the *M* series, lies on the line *xy*, fig. 1; the first digit denotes the chemical formula to be that of the correspondingly numbered body, table 5; the last digit indicates that the body was sent to the plant producing correspondingly numbered body, table 3.
[b] The feldspars used by the respective manufacturers, table 1.

The results of the factory tests substantiate in general the results obtained in the laboratory. One of the manufacturers reported a slight tendency toward jelling of casting bodies containing domestic kaolins and a somewhat slower rate of casting or filterpressing, as compared with bodies in regular use. The reports indicate that the substitution of domestic for English ball clay results in less shrinkage during drying and more during heat treatment, and a reduction, in some cases, of the plasticity and dry transverse strengths of the bodies. Terms used to describe the test bodies and their properties were "O. K.", "very fair", "quite satisfactory", and "good." However, in most

[6] J. Am. Ceram. Soc. 17, 262-267 (1934).

cases some modification would be required to make the test body entirely acceptable for replacement of the regular body. This fact was not surprising or discouraging since the ball clay contents of the test bodies had to be assumed, owing to lack of data, and the reports indicated that practically all the criticisms could be met by altering the amounts or types of ball clays in the test bodies.

V. DISCUSSION

1. METHOD OF EXPRESSING BODY COMPOSITIONS

The expression of whiteware body compositions in terms of feldspar, flint, and clay only can be very misleading. The minimum temperature required to vitrify a given body in this system could be changed 20 to 40° C by merely changing the raw materials used. For this reason the $RO–RO_2–R_2O_3$ system was used but, because of the necessity for considering the physical properties prior to heat treatment, it was found imperative that the clay content be at least approximately specified.

The compositions of the RO, RO_2, and R_2O_3 components of most whiteware body mixtures are comparatively uniform. It seems, therefore, valid to represent such bodies in terms of the $RO–RO_2–R_2O_3$ system except when auxiliary fluxes are used. There would probably be less error involved in treating the RO, RO_2, and R_2O_3 in ordinary whiteware bodies as though each were a pure chemical compound than to assume that the properties of all clays or of all feldspars are alike—an assumption which is inferred by the specification of body compositions merely in terms of feldspar, flint, and clay.

2. SUBSTITUTION OF DOMESTIC FOR IMPORTED CLAYS

Explanations of the adverse effects on certain physical properties when substituting a combination of Florida and North Carolina kaolins for English china clay may be found in the fact that bodies containing more than 6 or 8 percent of the Florida kaolin are difficult to deflocculate. Also, the North Carolina kaolin is difficult to vitrify, possibly because of the comparatively large particle size of the fluxing minerals present,[7] although its RO content is considerable.

The fact that the English china clay bodies were slightly less refractory than the Georgia kaolin bodies, as evidenced by their apparent porosities and bulk densities, may be due to:

1. Water vapor given off by the muscovite in the china clay reduces the vitrification temperature. The effect of water vapor on vitrification was reported by Badger.[8] (This vapor might attack the fluxing materials and make a greater portion of the RO content free to react readily in the formation of glass. This reaction would begin to take place well below the pce of feldspars and might help to explain the fact reported by Schramm and Hall [9] that a body containing a feldspar of high pce might mature at a lower temperature than one containing a feldspar of lower pce.)

2. Some form of magnesium which accelerates the formation of glass and which is present in china clay and not in kaolin. Experi-

[7] J. Am. Ceram. Soc. **18**, 163 (1935).
[8] J. Am. Ceram. Soc. **16**, 107 (1935).
[9] Am. Ceram. Soc. **19**, 159–168 (1936).

ment has shown that the minimum vitrification temperature of a body can be lowered approximately 5° C by incorporating 0.2 percent of magnesium carbonate in its formula.

3. COMMERCIAL BODIES AND THEIR SIMULATION IN THE LABORATORY

Of considerable interest is the difference between the chemical formulas of bodies now used in the industry and those which were considered as typical 8 or 10 years ago. The variations are shown in table 7.

TABLE 7.—*Comparison of bodies considered typical about 1930 with present commercial bodies*

Body	RO	RO_2	R_2O_3	Heat treatment[a], 1 hr at
	%	%	%	°C
SV (type)	2.5	74.3	23.2	1,225
P7	2.7	76.7	20.6	1,210
HT (type)	4.9	73.0	22.1	1,250
P3	6.3	69.7	24.0	1,235
P5	5.3	70.7	24.0	1,245
S (type)	4.2	72.4	23.4	1,270
P1	4.6	70.4	25.0	1,260
P6	4.8	72.2	23.0	1,255
V (type)	3.3	75.2	21.5	1,300
P4	4.9	73.1	22.0	1,250

[a] These minimum vitrification temperatures are based upon cast specimens containing no auxiliary fluxes, and the heating schedule employed (see p. 67). They are productive of maximum bulk specific gravity except in the cases of bodies *SV* and *P7*, which are semivitreous in type, having apparent porosities of about 12 percent.

In every case the commercial bodies tested contained more RO, making possible the same degree of vitrification with less severe heat treatment. The greatest difference is that between bodies *P4* and *V*.

The chief cause of the difference in the effect of a given heat treatment on a dry-pressed body as compared with the same body when cast is probably is the arrangement or packing of particles. There seems to be less difference between specimens formed by plastic processes and those made by casting methods.

The wide variation in clay content of the bodies of the *L* series and the comparatively small effect of this variation upon most of the properties tested is of general interest.

Comparison of the properties of bodies *L3* and *L5* (table 4) heated to 1,165° C with those of body *L7* heated to 1,210° C, shows the influence of RO content on the semivitrification temperature of whiteware.

4. EFFECT OF RO CONTENT ON VITRIFICATION

In the *M* series of bodies (located on the straight line *xy*, fig. 1), resorted to in the effort to correlate RO content of feldspathic whiteware bodies with vitrification temperature, there was a variation in total clay content of only 2.8 percent and changes in RO_2 and R_2O_3 contents of equal successive amounts with equal increments in RO content. It was thought that the RO_2/R_2O_3 ratio might have considerable effect on the properties of the bodies, but indications are that this ratio can vary rather widely without affecting the properties tested.

The curve in figure 2 is probably one of a family comprised of more or less parallel curves for cast bodies, for plastic-process bodies, and for dry-pressed bodies. The location of the curves for each of these bodies would be determined by heating rate or, possibly, the use of an auxiliary flux or of a water-vapor atmosphere. Very likely a decided change in composition of the RO (e. g., change from pure potash to pure soda feldspar) would affect the shape of that end of the curve, where the RO contents of the bodies are greater.

The location of a curve, such as shown in figure 2, is probably governed by the temperature or heat treatment required to form enough glass of sufficient fluidity to produce a continuous film throughout the bodies. The surface tension of this continuous film of glass draws the particles closer together, causing the pore spaces to be filled or closed. The fluidity of the glass film allows the particles to move into a more compact arrangement. At the end of the curve (fig. 2) representing greater RO content the fluxing materials present may furnish sufficient glass to cause vitrification without appreciable solution of the nonfluxing materials, while at the end of the curve representing less RO content the glass furnished by the fluxing materials must dissolve appreciable amounts of the nonfluxing materials in order to produce a sufficient quantity of glass which, being more viscous, requires a greater temperature to produce vitrification.

The percentage apparent porosity of the specimens (table 5) at maximum bulk specific gravity shows correlation with RO content, decreasing from 0.3 to 0.0 percent as RO increases from 2.7 to 4.9 percent.

The volume shrinkages during heating of the vitrified specimens vary only 0.6 percent, with the exception of bodies *M8*, *MG*, *EC*, and *MM*. The cause of these exceptions is easily traced through the bulk specific gravities of the dry specimens to the degree of dispersion of the slips. The relatively great feldspar content of body *M8* and the addition of excess deflocculant to the other three bodies probably caused the dispersion of these slips to be less complete. These results indicate the importance of the properties of the body prior to heat treatment.

Bodies *MG*, *EC*, and *MM* vitrified at the same temperature, which was about 5° C less than that indicated by the curve in figure 2 for bodies of their chemical formula.

Although bodies *V8* and *V9*, table 2, contain different feldspars, the one in *V8* having 11.7 percent of RO and a K/Na ratio of 3.4, and the one in *V9* having 14.7 percent of RO and a K/Na ratio of 6.2, they are, allowing for experimental inaccuracies, almost identical in every property tested. These results substantiate the findings of Geller and Creamer [10] and of Schramm and Hall.[11]

5. FACTORY TEST REPORTS

It is possible that the trouble which some cooperating manufacturers had with the casting bodies was due to incorrect amount or kind of deflocculant, since each undoubtedly used the kind he had on hand and may have been unable to spend sufficient time to determine the optimum amount required. At any rate, satisfactory casting slips of all the bodies tested by the manufacturers were made in the laboratory.

[10] J. Am. Ceram. Soc. **14**, 30 (1931).
[11] J. Am. Ceram. Soc. **19**, 159–168 (1936).

No insurmountable difficulty arising from the substitution of domestic kaolin for all of the imported china clay and of domestic ball clay for at least a portion (in some cases all) of the imported ball clay, was reported. In most cases such substitutions would apparently involve only minor adjustments in plant procedure which would not necessarily be difficult or costly.

The fact that practically all of the criticisms of the test bodies seem to be traceable to the ball clay would indicate that further study of the commercially available ball clays might be advisable.

VI. SUMMARY

Domestic kaolins and ball clays were substituted for imported clays in important types of whiteware bodies. Substitutions were based on the compositions, in terms of RO, RO_2, and R_2O_3 of the bodies and raw materials, and on the physical properties of the raw materials and those required of the bodies. Specimens were formed by casting and were tested in the dried and heat-treated conditions. Laboratory results indicated that the properties of imported-clay bodies could be duplicated by domestic-clay bodies. Factory tests indicated that in most cases both domestic ball clays and kaolins could replace imported clays with minor changes in plant procedure. In a few cases the use of a very plastic ball clay is required to give the body special properties. The results in general indicate that body properties are as dependent on the method of body preparation or of forming the ware as on the raw materials employed. The plasticity and dry strength of a feldspathic whiteware body prepared and formed by a given method depend chiefly on the type and amount of ball clay used, while the minimum vitrification temperature depends chiefly on its RO content. Both RO and ball clay contents of feldspathic whiteware bodies can be varied widely with little effect on the physical properties of the products after heating on similar schedules to the same degree of vitrification.

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NATURE OF THE ACID-DYEING PROCESS

By Arthur L. Smith and Milton Harris[1]

ABSTRACT

The dye-combining capacity of untreated wool has been determined for the typical acid dye, orange II, and shown to be equal to the acid-combining capacity. Treatments with nitrous acid, hydrogen peroxide, sodium hypochlorite, and strong solutions of sulfuric acid decrease the basicity of the wool and correspondingly decrease the affinity for acid dyes. Chlorinated wool absorbs acid dyes at a greater initial rate than untreated wool, but at equilibrium the latter absorbs more dye. The resist to acid dyes produced in the sulfuric-acid-carbonizing process is caused by the conversion of basic amino groups to sulfamic-acid derivatives. The results of the investigation constitute further evidence in favor of the chemical theory of acid dyeing.

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I. INTRODUCTION

The complexity of dyeing processes has given rise to many theories, all of which may be classified under the general headings of chemical or physical. However, the more recent work of Elöd [1],[2] Porai-Koschitz [2], Speakman [3], and their collaborators leaves little doubt that the reaction of wool with acid dyes is governed by chemical laws and consists in the neutralization of the basic groups in the fiber by the acidic groups of the dye molecules. The data in the present report, obtained by a somewhat different approach to the problem, constitute further evidence in favor of the chemical theory for this type of dyeing.

II. ACID-DYE-COMBINING CAPACITY OF UNTREATED WOOL

The majority of the investigations relating to the mechanism of the acid-dyeing process have been made under conditions which closely approximate those used in the commercial dyeing of wool. Unfortunately, the amount of dye required for such a dyeing constitutes only a small fraction of the total dye which the wool is capable of absorbing and, as a result, data from such investigations have little quantitative significance.

[1] Research Associates at the National Bureau of Standards, representing the American Association of Textile Chemists and Colorists. The work reported here was aided by grants from the Textile Foundation, Inc., and the Eavenson & Levering Co.

[2] Figures in brackets throughout the text correspond to the numbered references at the end of this paper.

Assuming that the acid-dyeing process consists in a reaction between the dye and the basic groups of the wool, then a given amount of wool should combine with equal molecular proportions of acid or acid dye. The acid-combining capacity of wool has been shown by several investigators [4, 5, 6, 7] to be about 0.80 millimole of acid per gram of wool, and it has also been shown [8] that the combined acid may be accounted for by the free amino groups and by the guanidine nucleus of the arginine in wool. The acid-dye-combining capacity of the wool was determined in the present investigation by the following procedure. Yarn, prepared from wool which had been solvent-scoured, was further purified by extraction in a Soxhlet apparatus with alcohol and with ether, and finally was washed in water at 140° F. The dye was a purified sample of orange II, analysis of which showed 90.6 percent of dye, 1.26 percent of sodium chloride, and 8.15 percent of moisture. The dyeings were boiled under a reflux condenser in a solution containing 1 millimole of dye per gram of wool, the ratio of wool to solution being 1:200. Sufficient sulfuric acid was added to obtain a pH of about 1.3, which is the pH shown by Elöd [1] to be necessary for the maximum absorption of acid dyes. The amount of dye absorbed from the solution was measured with a colorimeter by comparing the color of aliquots from the dye bath with that of solutions containing known amounts of the dye. The limiting absorption of dye appeared to be reached in 1.5 hours, when 0.85 millimole of dye per gram of wool had been absorbed. This value became slightly larger with increased time of dyeing, but on examination of the dye liquors, it was found that small particles of wool fibers were being split off.

This difficulty was readily overcome by lowering the temperature of the dye bath to 120° F, the only other effect being a considerable increase in the time necessary to reach equilibrium. The results of dyeing experiments at this temperature in a solution 0.1 *N* with respect to hydrochloric acid[3] are shown in table 1. Equilibrium appears to be reached after about 12 hours. All subsequent dyeings were done under these conditions for 18 hours in order to be well within the equilibrium region.

TABLE 1.—*Rate of absorption of orange II from a solution at 120° F containing 1 millimole of dye per gram of wool, the ratio of wool to solution being 1:200*

Time	Amount of orange II absorbed
Hours	*Millimole per gram of wool*
2	0.28
3.3	.38
5	.63
8	.71
9	.73
12	.81
21.3	.85
22	.82

[3] The pH of the dye bath was maintained with 0.1 *N* HCl, because in subsequent experiments, it was necessary to find out whether sulfuric acid was split off from wool which had previously been treated with concentrated solutions of sulfuric acid.

The results of a similar set of equilibrium dyeings, using 0.5, 1.0, and 1.5 millimoles of dye per gram of wool, are recorded in table 2 and show that the amount of dye absorbed is independent of the concentration, providing sufficient dye is present to react with all of the basic groups in the fiber.

The solution was 0.1 *N* with respect to hydrochloric acid.

TABLE 2.—*Effect of varying the concentration of the dye bath on the amount of dye absorbed by wool at equilibrium*

Concentration of orange II in dye bath	Amount of orange II absorbed
Millimoles per gram of wool	*Millimoles per gram of wool*
0.50	0.49
1.00	.83
1.50	.82

The values of 0.82 and 0.83 millimole of orange II absorbed per gram of wool are in good agreement with the acid-combining capacity and with the value 0.8 obtained by Porai-Koshitz [2] who used the dye eosine. He worked with the ammonium salts and showed that the amount of ammonia liberated corresponded to the amount of dye absorbed.

III. EFFECT OF VARIOUS TREATMENTS ON THE ACID-DYE-COMBINING CAPACITY OF WOOL

1. EFFECT OF NITROUS ACID

One of the arguments that has been repeatedly used against the chemical theory of acid dyeing is based on what appears to be the unchanged affinity for acid dyes of wool treated with nitrous acid. Trotman [9], Paddon [10], and Benz and Farrell [11] attempted to destroy this affinity by deamination of the wool, and all concluded that treatment of wool with nitrous acid had little if any effect on the absorption of acid dyes by the fiber. All of these workers failed to realize that deamination, even when produced by prolonged treatment with nitrous acid, only partially destroys the basic properties of wool [3, 8]. In addition, they used amounts of dyes which would be readily taken up by the remaining basic groups in the wool.

More recently, however, Speakman and Stott (3) working with high concentrations of dyes and samples of wool which had been treated with nitrous acid for nearly 100 hours, demonstrated that the affinity of deaminated wool for acid dyes is far less than that of untreated wool. The results they obtained were confirmed by similar experiments in the present investigation, under far less drastic conditions of deamination. A sample of wool yarn was treated with a 10-percent solution of nitrous acid at room temperature for 3 hours, after which it was washed for 48 hours in distilled water. The treated sample had acid- and acid-dye-combining capacities of 0.5 and 0.4 millimole per gram, respectively.

2. EFFECT OF HYDROGEN PEROXIDE

In an investigation of the effect of hydrogen peroxide on the basic groups in wool [12], it was found that the acid-combining capacity decreased with increased oxidation. The magnitude of these changes was so great as to suggest a similar determination of the acid-dye-combining capacity. Samples of wool were oxidized for different lengths of time with a 3-percent neutral solution of hydrogen peroxide at 120° F. The effect of the treatment on the basic properties of the wool is shown in table 3. Both the acid- and the acid-dye-combining capacities decrease at about the same rate with increase in time of oxidation.

TABLE 3.—*Effect of oxidizing wool with 3 percent of hydrogen peroxide at 120° F for different lengths of time on the acid- and the acid-dye-combining capacities*

Duration of oxidation	Acid-dye-combining capacity	Acid-combining capacity
Hours	*Millimole per gram*	*Millimole per gram*
0	0.78	0.77
3	.77	.73
7	.68	.60
16	.52	.43
24	.54	.44
43	.34	.33

3. AFFINITY OF CHLORINATED WOOL FOR ACID DYES

Treatment of wool with chlorine or bromine has been claimed by various workers [13] to increase the dye-absorbing capacity of wool. Such claims appear to contradict the well-known ease of oxidation of amino groups by halogens [14] as well as the findings of the present investigation, which show that the acid-combining capacity of wool treated with a sodium hypochlorite solution (containing at pH8, 8 percent of active chlorine, based on the weight of the wool) decreases from 0.79 to 0.71 millimole. This apparently anomalous behavior of halogenated wool is readily explained by the determination of the rate of absorption of acid dye by untreated wool and by wool treated with the sodium hypochlorite solution containing 8 percent of active chlorine. The curves in figure 1 show that the initial rate of absorption of dye is much higher for the chlorinated sample, but that at equilibrium slightly more dye is taken up by the untreated sample. The increased rate of absorption of the dye appears to be caused in part by changes in the physical structure of the fiber during chlorination, a factor previously noted by Trotman [16].

4. NATURE OF THE RESIST PRODUCED IN WOOL BY THE CARBONIZING PROCESS

After treatment by the carbonizing process, wool exhibits a decreased affinity for acid dyes and a correspondingly increased affinity for basic dyes. Since a large portion of commercial wool is dyed with acid dyes, this alteration of the affinity of the fiber for dyes is commonly referred to as a resist, although strictly speaking, it is only a resist to acid dyes. The factors which influence the formation of the resist on wool have been pointed out by Ryberg [16].

The present studies on the nature of the acid-dyeing process indicated that the resist was probably formed by decreasing the basic properties of the fiber. However, a mechanism which would account for the decrease in the basicity during carbonizing was not suggested until recently when Harris, Mease, and Rutherford [17] showed that, in addition to a reversible reaction of wool with sulfuric acid, there was a possible irreversible reaction. These are shown in the following equations:

$$RNH_2 + H_2SO_4 \rightleftharpoons RNH_3.HSO_4 \quad (1)$$

$$RNH_2 + H_2SO_4 \rightarrow RNHSO_3H + H_2O, \quad (2)$$

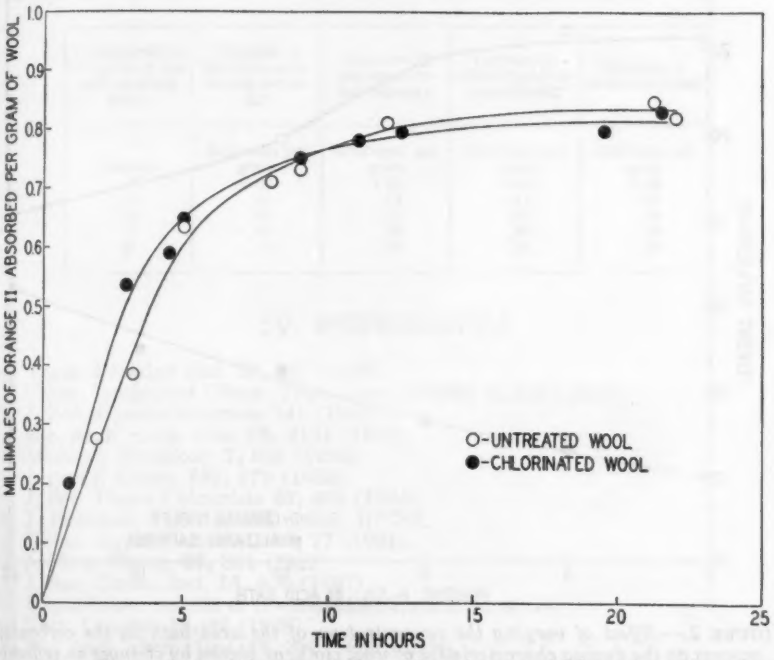

FIGURE 1.—*Comparison of the rate of absorption of orange II by untreated wool with that by wool which had been treated with a sodium hypochlorite solution containing 8 percent of active chlorine based on the weight of the wool.*

where R represents the portion of the wool to which the basic group is attached.

Equation 1 indicates the reaction which is assumed to take place in dilute solutions of sulfuric acid. The acid in the compound formed in this reaction is reversibly held and is readily replaceable by acid dyes. On the other hand, the reaction represented in equation 2 appears to take place only under dehydrating conditions, for example, in the presence of strong solutions of sulfuric acid. The reaction of basic groups in wool with sulfuric acid, to form sulfamic acid derivatives according to equation 2, not only decreases the basic properties but also increases the acidic properties.

The results of that work immediately suggested that a similar reaction might occur in the carbonizing process, and would not only account for the decreased affinity for acid dyes but also for the increased

affinity for basic dyes. Although the concentration of sulfuric acid in the acid-soaking bath seldom exceeds 5 percent by weight, the acid becomes concentrated on the fiber during the subsequent drying and baking processes and the reaction in equation 2 could occur.

That the formation of the resist is the result of producing a new compound of the sulfamic acid type is demonstrated by the following experiment. Samples of wool cloth were soaked for 15 min at 70° F in solutions of sulfuric acid, varying in concentration up to 20 percent by weight. The samples were immediately centrifuged to about 40 percent of condition, baked 15 minutes at 250° F, and washed in running distilled water for about a week. The decrease in the acid-

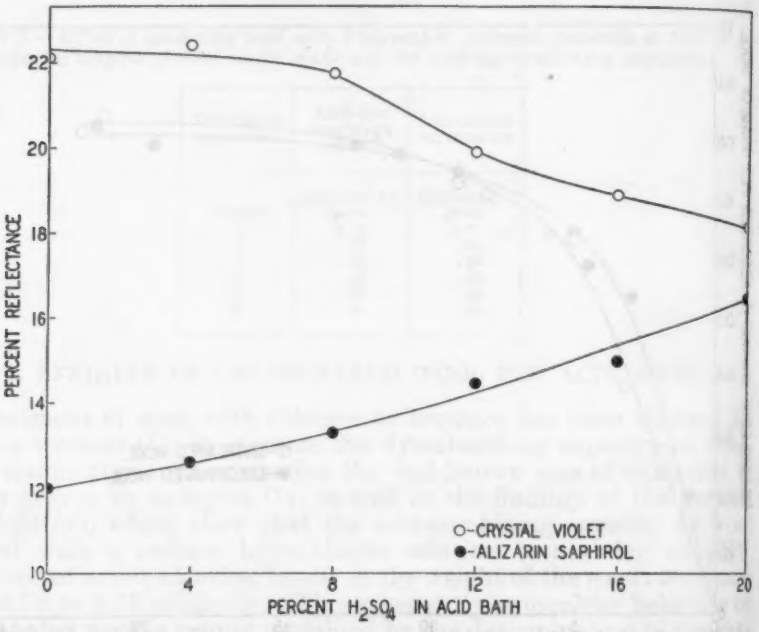

FIGURE 2.—*Effect of varying the concentration of the acid bath in the carbonizing process on the dyeing characteristics of wool cloth, as shown by changes in reflectance of light at wave length 436 millimicrons for the samples dyed with crystal violet, and wave length 501 millimicrons for those dyed with alizarin saphirol.*

and acid-dye-combining capacities and the increase in the alkali-combining capacity [17] and the sulfate content [18] with increasing concentration of acid in the soaking bath are shown in table 4. Although good agreement between the decrease in acid-combining capacities and the increase in alkali-combining capacities and sulfate content was obtained, the decrease in the acid-dye-combining capacity is low. This discrepancy was accounted for when an examination of the dye baths showed the presence of sulfate. This indicated that hydrolysis of the sulfamic acid groups had occurred during the prolonged dyeing, thus regenerating some basic amino groups.

The data in table 4 also show that a large proportion of the basic groups in wool are still available for dyeing. Since the number of moles of dye per gram of wool used in commercial dyeings is very much smaller than the residual acid-dye-combining capacities, the

visual differences in the color of commercially dyed, carbonized samples indicates that the bulk of the resist is formed on the surface of the fiber. The effect of varying the acid concentration of the soaking bath, as previously described, on dyeings which approximate those obtained commercially is shown in figure 2. Here the formation of the resist, as evidenced by the increase in reflectance of the samples dyed with alizarin saphirol, is accompanied by a corresponding increased affinity for basic dyes, as shown by the decrease in reflectance of the samples dyed with crystal violet.

TABLE 4.—*Effect of varying the concentration of acid in the soaking bath used in the carbonizing process on the acidic and basic properties of wool*

Concentration of H_2SO_4 in the acid soaking bath	Decrease in acid-dye-combining capacity	Decrease in acid-combining capacity	Increase in alkali-combining capacity	Increase in sulfate content
Percent	*Millimole per gram*	*Millimole per gram*	*Millimole per gram*	*Millimole per gram*
4	0.00	0.01	0.04	0.02
8	.01	.13	.11	.09
12	.08	.21	.23	.16
16	.08	.24	.30	.18
20	.11	.26	.34	.28

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[18] J. Research NBS **13,** 617 (1934) RP731.

WASHINGTON, May 18, 1937.

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EXTENSION OF NORMAL-INCIDENCE IONOSPHERE MEASUREMENTS TO OBLIQUE-INCIDENCE RADIO TRANSMISSION

By Newbern Smith

ABSTRACT

A simple, rapid graphical method is given for obtaining skip distances and limiting frequencies for radio waves, from normal-incidence measurements. The applications of the method are outlined.

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I. INTRODUCTION

It is possible to interpret certain aspects of long-distance radio-transmission conditions in terms of normal-incidence ionosphere measurements of virtual heights and critical frequencies. It is the purpose of this note to outline a simple, rapid graphical method of obtaining, from these normal-incidence measurements, skip-distance, maximum usable frequency over a given path, and virtual heights of reflection of waves incident obliquely upon the ionosphere. This method has been used at the National Bureau of Standards since the beginning of 1936 for interpreting radio-transmission data in terms of the regular ionosphere measurements. More recently it has been used in preparing the data for the weekly broadcasts of radio-transmission conditions, in interpreting low-layer ionosphere transmission, and in supplementing local ionosphere measurements by data obtained from observations of long-distance transmission. Part of this work was presented as a paper at the 1936 joint meeting of the Institute of Radio Engineers and International Scientific Radio Union at Washington.[1]

II. THEORY

Breit and Tuve's theorem [2] states that in the absence of dissipation a wave traversing a trajectory in the ionosphere undergoes the same group retardation as a wave traversing with the velocity of light a triangular path of the same base as the actual path and with the same angle of incidence on the ionosphere.

[1] N. Smith, S. S. Kirby, and T. R. Gilliland. *Recent correlations between the ionosphere and high-frequency radio transmission.* Paper before joint meeting of IRE and URSI, May 1, 1936. To be published in J. Research NBS and Proc. Inst. Radio Engrs.

[2] G. Breit and M. A. Tuve, Phys. Rev. **28**, 554 (1926).

The process of refraction and reflection of a radio wave in the ionosphere depends on the variation of the refractive index μ of the medium with the ionization density N. From the elementary theory of propagation of electromagnetic waves in a medium of varying refractive index, it follows that the wave will penetrate the medium only until the refractive index is reduced to the value sin ϕ_0, where ϕ_0 is the angle of incidence of the wave on the ionosphere (see fig. 1), that is, to the level z_0. For the normal incidence case, this means that reflection takes place at the level where $\mu=0$.

Breit and Tuve's theorem states implicitly that if reflection takes place at a level z_0, the virtual height z_v, or height of the equivalent triangular path, is constant regardless of the value of ϕ_0. If we assume the validity of this theorem, therefore, it follows that the virtual height measured at normal incidence for a frequency f that makes $\mu=0$ for some value of N, will also be the virtual height attained in transmission over a distance by a wave of a different frequency f', such that $\mu=\sin\phi_0$ for this same value of N.

Instead of using the ionization density N, we shall use a quantity f_0, of the nature of a frequency and defined as

$$f_0=\sqrt{\frac{Ne^2}{\pi m}}$$

Using this quantity and the quantities f_T and f_L, which represent, respectively, the frequencies of precession of electrons in the components of the earth's magnetic field transverse to and along the direction of phase propagation, we may write the Appleton-Hartree formula [3] for the refractive index of a nondissipative ionized medium in the presence of the earth's magnetic field, for a radio wave of frequency f':

$$\mu^2=1-\frac{f_0^2}{f'^2-\frac{f'^2f_T^2}{2(f'^2-f_0^2)}\pm\sqrt{\left[\frac{f'^2f_T^2}{2(f'^2-f_0^2)}\right]^2+f'^2f_L^2}}$$

The refractive index vanishes for $f_0=f'$ and $f_0^2=f'(f'\pm f_H)$ where $f_H^2=f_T^2+f_L^2$. The component of the wave reflected at normal incidence from the level where $f_0=f'$ is known as the ordinary component, and the one reflected from the level where $f_0^2=f'(f'\pm f_H)$ is known as the extraordinary component. Usually the extraordinary component is reflected mostly from only one of these levels (the one where $f_0^2=f'(f'-f_H)$ for $f'>f_H$ and the one where $f_0^2=f'(f'+f_H)$ for $f'<f_H$).

By using the Appleton-Hartree formula with f_T and f_L evaluated at the top of the wave path, where the direction of propagation is horizontal, and setting $\mu=\sin\phi_0$, we may obtain a set of values of f_0 and ϕ_0, for a given value of f', representing transmission conditions at a given frequency. It is possible to express f_0 in terms of a frequency f of a wave at normal-incidence for either the ordinary or extraordinary components by using the above relations, and it is possible to express ϕ_0 in terms of virtual height z_v and distance of transmission D (fig. 1), by a purely geometrical relation. We can thus obtain a set of values of normal-incidence equivalent frequencies

[3] E. V. Appleton, J. Inst. Elec. Engrs. (London) 71, 642 (1932).

f and virtual heights z_v, representing radio-transmission conditions for a given frequency f' over a given distance D.

III. TRANSMISSION CURVES

If, in normal incidence measurements, a wave of frequency f is returned from a virtual height equal to the z_v computed for a given distance and transmission frequency f', the wave of frequency f' will be reflected from a region of ionization density equal to that for which $\mu=0$ for the frequency f and its equivalent triangular ray path will correspond to this virtual height, by Breit and Tuve's theorem. This point of reflection may be readily determined as the intersection of a normal-incidence frequency–virtual-height curve of the type obtained in multifrequency ionosphere experiments, with a curve plotted from the set of values of f and z_v obtained for a given f' and D. This latter curve may be called a transmission curve for the given frequency and distance.

This development is valid both for ordinary and extraordinary rays. For the ordinary ray, the transmission curve is, at least in

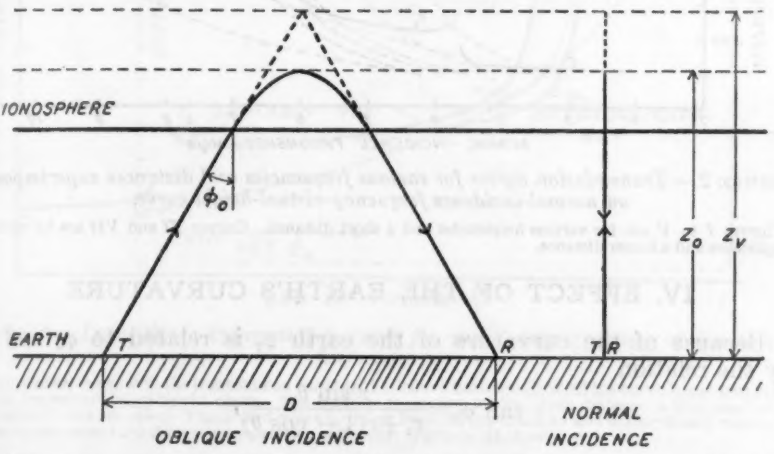

FIGURE 1.—*Normal-incidence and oblique-incidence ionosphere transmission*

T is the transmitter, and *R* is the receiver. The solid line is the actual path taken by the waves and the dotted line shows the equivalent triangular path.

these latitudes, very nearly a "secant-law" curve, i. e., $f=f'/\sec\phi_0$. In computing the transmission curve for the ordinary ray the virtual height for the oblique-incidence case is that for the ordinary ray component of frequency f at normal incidence, and corresponds to the frequency f_0. This ionization density is used in computing ϕ_0, and the transmission curve is applied to the ordinary ray frequency–virtual-height curve. The extraordinary component can be treated similarly.

The solid curve in figure 2 is a typical frequency–virtual-height curve for the ordinary component, showing E and F_2 layers. Superimposed on it are the dotted transmission curves for various frequencies and distances. Curves *I*, *II*, *III*, *IV*, and *V* are for increasing frequencies and for a fairly short distance. For the frequency corresponding to *I*, transmission is by way of E layer. For curve *II*

the given distance is within the skip zone for *E*-layer transmission, but is transmitted by F_2 layer. Curve *III* shows transmission by two paths (high and low virtual heights), as reported in various papers.[4] Curve *IV* corresponds to the maximum possible frequency that can be used over the given distance. As the F_2 critical frequency varies, transmission has been observed to begin and fail quite abruptly at this point. For curve *V* the frequency is too high and the given distance is within the skip zone for any ordinary-ray transmission. Curves *VI* and *VII* are for a longer distance, and show a condition where *E*-layer transmission takes place at higher frequencies than *F*-layer transmission. Curve *VII* shows the skip effect again.

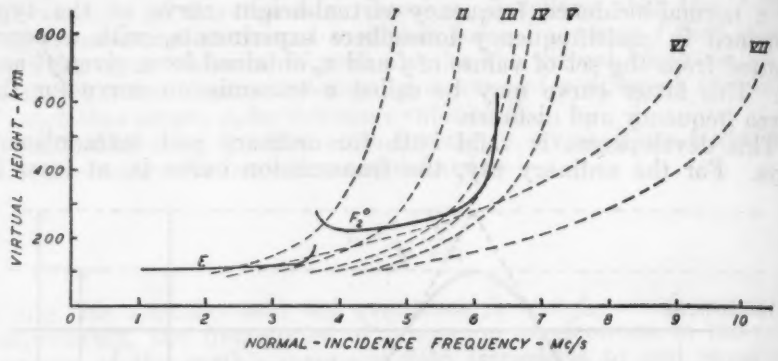

FIGURE 2.—*Transmission curves for various frequencies and distances superimposed on normal-incidence frequency–virtual-height curve.*

Curves *I* to *V* are for various frequencies and a short distance. Curves *VI* and *VII* are for various frequencies and a longer distance.

IV. EFFECT OF THE EARTH'S CURVATURE

Because of the curvature of the earth z_0 is related to ϕ_0 and D by the relation

$$\tan \phi_0 = \frac{r \sin \theta}{z_0 + r(1 - \cos \theta)},$$

where r = radius of earth in kilometers
$\theta = 222.4/D$ degrees
D = distance in kilometers.

Although Breit and Tuve's theorem is strictly true only for a plane earth, and there is some doubt as to its strict validity in the presence of the earth's magnetic field, experiment shows a remarkable agreement between skip distances observed and those calculated using this method. Because of penetration of the ionosphere the angle of incidence ϕ_0 is not quite the same as that computed from the geometrical relation above, and the virtual heights used must be smaller than those measured, for the greater distances. Any difference in skip distance arising from this effect is probably less than the uncertainty in the characteristics of the ionosphere at latitudes and longitudes other than those where the ionosphere measurements are made.

[4] F. T. Farmer and J. A. Ratcliffe, *Wireless waves reflected from the ionosphere at oblique incidence.* Proc. Phys. Soc. 48, 839 (1936).
W. Crone, K. Krüger, G. Goubau, and J. Zenneck, *Echo measurements over long distances.* Hochfrequenztechnik u. Elektroakustik 48, 1 (1936).

V. APPROXIMATE METHOD OF CALCULATION

For rapid approximate calculation, use may be made of the fact that the transmission curve for the ordinary ray is very nearly a secant-law curve, and of the fact that as the distance of transmission is increased, the separation of the ordinary and extraordinary limiting frequencies decreases rapidly. For this purpose, the frequency–virtual-height curve is plotted on semilogarithmic paper, the frequencies being plotted logarithmically. Transmission curves for various distances are plotted semilogarithmically on transparent paper as virtual heights vs. reciprocals of sec ϕ_0. The reciprocals of sec ϕ_0 are used, since it is necessary to divide the transmitted frequency by sec ϕ_0 to obtain the

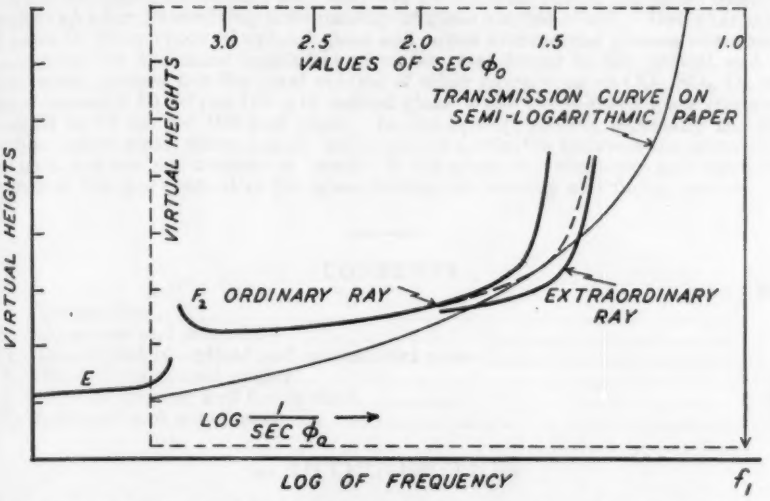

FIGURE 3.—*Logarithmic transmission curve for rapid determination of limiting frequency*

The transparent paper with the transmission curve on it is moved horizontally until the curve is just tangent to the frequency-virtual-height curve. The limiting frequency for the given distance is then read off opposite the line sec $\phi_0=1$. The dotted curve is drawn between the ordinary and extraordinary rays in order to take care of the decreasing separation of the rays at greater distances.

equivalent normal-incidence frequency. The transmission curves are then superimposed on the frequency–virtual-height curve for the ordinary component, as shown in figure 3, and moved until the transmission curve for the desired distance is just tangent to the frequency–virtual-height curve. The frequency corresponding to sec $\phi_0=1$ (marked f_1 in fig. 3) is then the maximum usable frequency for that distance. For a closer approximation, the frequency–virtual-height curve may be corrected by drawing an estimated transition curve between the ordinary and extraordinary components, as shown by the thin dashed line in figure 3. This will give better values for short distances. This method is being used in preparing data for the weekly ionosphere broadcasts of the National Bureau of Standards.

A discussion of radio transmission and the ionosphere is being published in the June issue of the Journal of Research of the National Bureau of Standards and in the Proceedings of the Institute of Radio Engineers, and is available in the form of a Letter Circular of the National Bureau of Standards.

A type of transmission curve based on the principles described above, was developed independently by L. V. Berkner, of the Department of Terrestrial Magnetism, Carnegie Institution of Washington, and described by him at the joint meeting of the IRE and URSI at Washington, on April 30, 1937.

WASHINGTON, May 28, 1937.

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RESEARCH PAPER RP1014

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GASES IN SOME OPTICAL AND OTHER GLASSES

By Clarence Hahner, George Q. Voigt, and Alfred N. Finn

ABSTRACT

An apparatus and method for removing by vacuum fusion the gases dissolved in glass and for determining the quantity of gases are described. Determinations of gases in three types of optical glass and seven commercial glasses were made. Approximately the same quantities of water were found in the optical and the commercial glasses, but the total volume of other gases, such as CO_2, SO_2, O_2, etc., never exceeded 10 ml per 100 g of optical glass, while the window glass contained from 34 to 73 ml per 100 g of glass. In the optical glasses, especially the light barium crown glass, there was no indication of a relation between the quantity of gas obtained and the number of "seeds" in the glass, nor was there any significant change in the gas content of the glass during the stirring and fining periods.

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I. INTRODUCTION

It has been known for some time that all ordinary glasses when fused in a vacuum will yield gases that are either dissolved in the glass or formed by the decomposition of compounds that exist in the glass. This paper constitutes a report on the determination of the amounts and kinds of gases found in optical glasses and their bearing on the presence of "seeds" or small bubbles in the finished glass. Also, for comparison, the gases in some window glasses and tubing were determined.

Summaries of the methods for the determination of gases in glass, and the history of their development have been published by Dalton.[1] and also by Salmang and Becker [2] within the past few years. In all of the work that has been done on the extraction of gas from molten glass, the chief source of uncertainty has been the magnitude of the errors introduced by the absorption of gases by the alkaline materials that are volatilized from the molten glass. No method of eliminating this uncertainty has thus far been proposed, and little has been said as to just how large the error might be. The problems encountered in this respect are of major importance in the proper consideration of the results obtained.

[1] R. H. Dalton. *Gases in glass.* J. Am. Ceram. Soc. **16,** 425 (1933); *Extraction and analysis of gases from glass.* J. Am. Chem. Soc. **57,** 2150 (1935).
[2] H. Salmang and A. Becker. Glastech. Ber. **5,** 520 (1928); **6,** 625 (1929); **7,** 241 (1929).

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II. APPARATUS AND PROCEDURE

A diagrammatic sketch of the apparatus is shown in figure 1.[3] The apparatus consisted of a furnace in which the glass could be melted in a vacuum, an automatic sample-collecting pump of a type developed by Weaver and Shepherd,[4] a weight burette [5] for determining the volume of gas by weighing a quantity of mercury having an equal volume, and an Ascarite tube for absorbing the CO_2.

The automatic sample-collecting pump consisted essentially of a mercury-vapor pump, a McLeod gage so arranged that it could be used to measure the pressure on either the high- or low-pressure side of the vapor pump, and an automatic Töpler pump for collecting the gas. Since the Töpler pump cannot be used to pump vapors that are readily condensable at room temperature, a weighing tube containing

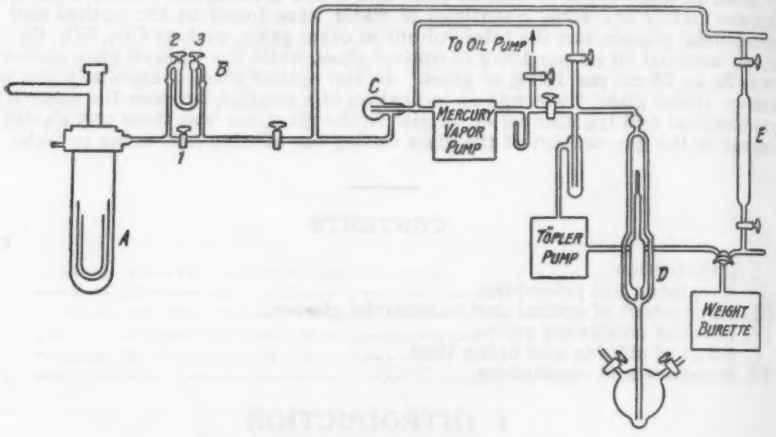

FIGURE 1.—*Sketch of vacuum system.*

A, vacuum furnace; *B*, weighing tube filled with Dehydrite; *C*, drying bulb filled with Dehydrite; *D*, McLeod gage; *E*, Ascarite tube.

Dehydrite was placed between the furnace and the pump to absorb the water vapor.

A detailed sketch of the furnace is shown in figure 2. It consisted of a transparent fused-silica tube (24 cm long and 6 cm in diameter), inside of which was a smaller silica tube (12 by 4.5 cm); inside the latter was the platinum crucible in which the glass was melted. The crucible and the two silica tubes were separated from each other by means of fused-silica supports.

The larger silica tube was closed at the top by a water-cooled brass cap having a fused-silica window in the top and a tube at the side to hold the glass sample and a piece of iron rod (*A*, fig. 2) during preliminary heating and degassing of the furnace. The iron rod, which could be actuated by a magnet, was used to push the glass forward until the sample dropped into the crucible.

[3] Since this apparatus was constructed, Dalton described in the Journal of the American Chemical Society (see footnote 1) an apparatus which, because it has no stopcocks or greased or cemented joints in the part of the system used for collecting and analyzing the gases, should be free from some of the difficulties encountered in manipulating the apparatus described in this paper.

[4] E. R. Weaver and M. Shepherd. *An automatic sample-collecting vacuum pump.* J. Am. Chem. Soc. **50**, 1829 (1928).

[5] E. R. Weaver and P. G. Ledig. *A weight burette for gas analysis.* J. Am. Chem. Soc. **42**, 1177 (1920).

The platinum crucible (9 by 3.7 cm) had a capacity of 100 ml. This rather large capacity was necessary because of the frothing that took place when the glass was heated in a vacuum. As the heating was done by means of high-frequency induction, it was necessary that the walls of the platinum crucible be rather thick to prevent localized heating and consequent failure of the crucible. The walls of the crucible were about 1 mm in thickness.

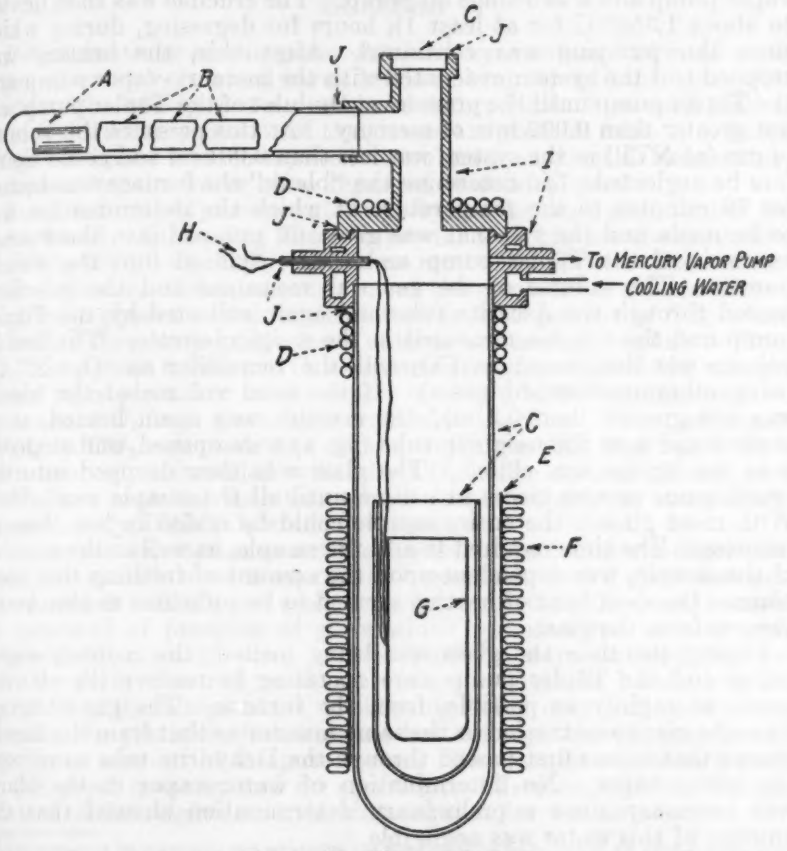

FIGURE 2.—*Vacuum furnace.*

A, iron rod; *B*, sample; *C*, fused silica; *D*, copper tubing for cooling water; *E*, sheet mica cylinder; *F*, inductor coil; *G*, platinum crucible; *H*, thermocouple; *I*, tinned brass cap and collar; *J*, Cementyte seals.

Energy for heating the platinum crucible was supplied by an Ajax 3 kva high-frequency converter and an inductor coil consisting of 50 turns of flattened copper tubing through which cooling water was circulated. The temperature was measured by a platinum–platinum–10-percent-rhodium thermocouple. To insure good thermal contact, both wires of the thermocouple were welded directly to the platinum crucible.[6]

The operation of the apparatus can best be explained by following through the steps of a typical analysis. The weighed sample, which

[6] An attempt was made to determine the temperature of the glass with an optical pyrometer, but this was not successful because volatile oxides from the hot glass condensed on the window.

consisted of five to eight pieces of glass (usually in the form of a rod), was cleaned with distilled water and alcohol, and heated to about 500° C in an electric muffle furnace to insure complete drying. Immediately after the sample was cold, it was placed in the sample tube, and the cap was sealed to the silica tube by means of Cementyte cement.

The furnace and the system were then evacuated, using the mercury-vapor pump and a two-stage oil pump. The crucible was then heated to about 1,350° C for at least 1½ hours for degassing, during which time the pumping was continued. After this, the heating was stopped and the system evacuated with the mercury-vapor pump and the Töpler pump until the pressure at the inlet of the Töpler pump was not greater than 0.002 mm of mercury. At this pressure the volume of gas (at NTP) in the system was less than 0.001 ml and could therefore be neglected. To determine the "blank" the furnace was heated for 30 minutes to the temperature at which the determination was to be made and the gas that was given off pumped into the storage reservoir of the Töpler pump and then displaced into the weight burette. The volume of the gas was measured and the gas then passed through the Ascarite tube and again collected by the Töpler pump and the volume measured in the weight burette. The loss in volume was designated as CO_2 and the remainder as "O_2+R" (R being other unabsorbed gases). If the total volume of the blank, was not greater than 0.2 ml,[7] the crucible was again heated, stopcocks 2 and 3 on the weighing tube (fig. 1) were opened, and stopcock 1 in the bypass was closed. The glass was then dropped into the crucible one or two pieces at a time until all the sample was added. With most glasses the entire sample could be added in less than 15 minutes. The time required to add the sample, as well as the amount of the sample, was dependent upon the amount of frothing that took place. One-half hour of heating seemed to be sufficient to remove all the gas from the glass.

During the time the glass was being melted, the mercury-vapor pump and the Töpler pump were operating to remove the evolved gases, as rapidly as possible, from the furnace. The gas obtained from the glass was treated in the same manner as that from the blank, except that it was first passed through the Dehydrite tube to remove the water vapor. No determination of water vapor in the blank was necessary since a preliminary determination showed that the amount of this water was negligible.

After the furnace had been cut off from the rest of the system, the stopcocks on the weighing tube were closed, and the weighing tube was removed. The grease was carefully cleaned off the ground-glass joints with petroleum ether and then with absolute alcohol, and the tube was weighed, using for a counterpoise a tube of like dimensions. The tube had been evacuated, cleaned, and weighed in a similar manner before the determination was started.

Before work was started on the glasses, some control determinations were made. A known quantity of H_2O was added to the system by dropping a small thin-walled glass bulb containing a weighed quantity of water into the hot crucible. In two cases, 22.4 and 10.8 mg of H_2O were added and 21.1 and 10.6 mg were found. A known quantity

[7] Although the furnace was degassed for 1½ hours, it was sometimes necessary to further degas the furnace until a satisfactory blank was obtained. When the value of the blank was 0.2 ml or less, it was but little reduced by further degassing up to 3 hours.

of CO_2 was added to the system by dropping a weighed piece of calcite into the crucible. In two cases, calcite equivalent to 4.40 and 4.09 ml of CO_2 was added and 4.41 and 4.12 ml were found. These determinations were made under the same conditions as those used when a determination was made with a glass sample.

III. GAS CONTENT OF OPTICAL AND COMMERCIAL GLASSES

Determinations of the gases obtained by vacuum fusion of three types of optical glass and seven kinds of commercial tank glass were made. The averages of a number of determinations on each kind of glass and the compositions of the glasses are given in table 1, in which all gas volumes were computed to volumes at normal temperature and pressure, the water being regarded as an ideal gas.[8]

In all the optical glasses water was by far the most abundant of the gases found. In most of the commercial tank glasses the quantities of "CO_2+SO_2" and "O_2+R" were materially greater than in the optical glasses. Chemical analyses of the commercial glasses showed that these glasses contained from 0.19 to 0.50 percent of SO_3, which indicated they were made from batches containing sulphate. Since SO_3 decomposes to SO_2 and O_2 at the temperature at which the vacuum fusion takes place, one might expect to obtain both SO_2 and increased amounts of O_2 from glass made from such batches. No separation of SO_2 from CO_2 was made and consequently any SO_2 that might have been evolved is included with the CO_2. The optical glasses were made from material that was almost free from sulphur compounds. Consequently, little SO_2 would be expected.

To determine whether or not the amount of gas found was dependent upon the surface area, a sample of borosilicate crown glass was prepared, which had a much greater surface area than the usual sample. It consisted of particles of glass which passed a no. 10 and were retained on a no. 20 sieve. These particles were sintered together into the form of a rod so that the sample could be handled in the equipment, the temperature of sintering being only sufficiently high to make the particles stick together but not high enough to close any significant amount of the pore spaces. The sample was then treated in the usual manner, and no significant difference between the gas content of the original and the sintered samples was noted.

[8] The apparatus for measuring and separating the gases could be made smaller for more accurate work since the volumes of gases obtained were less than was anticipated.

TABLE 1.—*Average values for volumes of gases obtained from glasses and composition of the glasses*

Glass [1]	Temperature of outgassing	Gas per 100 g of glass			Composition of glass [2]													
		H_2O	O_2+R	CO_2+SO_2	SiO_2	CaO	MgO	Na_2O	K_2O	R_2O_3	B_2O_3	ZnO	BaO	As_2O_5	As_2O_3	Sb_2O_3	SO_3
	°C	ml	ml	ml	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
OPTICAL GLASSES																	
Borosilicate crown *A* (2)	1,325	49	0.2	<0.1	65.6	-------	-------	7.9	12.8	-------	11.4	1.8	-------	0.40	0.03	-------	-------
Borosilicate crown *B* (3)	1,345	29	0	0	65.6	-------	-------	7.9	12.8	-------	11.4	1.8	-------	-------	.5	-------	-------
Light barium crown *A* (2)	1,350	20	1.0	0	47.1	2.1	-------	1.9	7.7	-------	4.3	8.5	27.9	.53	.01	-------	-------
	1,325	31	.8	0													
Light barium crown *B* (3)	1,345	21	1.2	.7	46.6	-------	-------	.5	7.1	-------	3.7	7.8	33.7	-------	.6	-------	-------
Light barium crown *C* (2)	1,345	17	1.1	<.1	46.9	-------	-------	.5	7.1	-------	3.7	7.9	33.2	-------	.2	0.5	-------
Light crown *A* (4)	1,300	33	1.7	4.0	71.0	13.1	-------	15.4	-------	-------	-------	-------	-------	.31	.01	-------	-------
Light crown *B* (1)	1,350	38	5.4	4.1	71.0	13.1	-------	15.4	-------	-------	-------	-------	-------	-------	.5	-------	-------
COMMERCIAL GLASSES																	
Window glass *A* (2)	1,345	16	10.2	43.1	72.1	10.0	3.3	13.5	-------	0.7	-------	-------	-------	-------	-------	-------	0.35
Window glass *B* (2)	1,345	28	17.1	17.0	72.6	8.0	3.6	15.0	-------	.7	-------	-------	-------	-------	-------	-------	.47
Window glass *C* (2)	1,345	22	32.5	26.6	73.1	13.3	.3	12.4	0.1	1.0	-------	-------	-------	-------	-------	-------	.44
Window glass *D* (2)	1,345	26	22.2	51.2	70.9	11.2	4.4	12.2	.1	.9	-------	-------	-------	-------	-------	-------	.41
Window glass *E* (3)	1,345	32	7.9	40.2	71.5	10.6	1.8	15.0	.2	.9	-------	-------	-------	-------	-------	-------	.45
Window glass *F* (2)	1,345	26	3.3	40.4	72.3	10.0	1.0	15.1	.3	.6	-------	-------	-------	-------	-------	-------	.50
Soda-lime tubing [3] (6)	1,345	23	3.0	14.0	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	.19

[1] The letters in this column indicate separate melts of glass in the optical group and glasses from different factories in the commercial group. The number in parentheses indicates the number of determinations on which the average is based.

[2] The compositions of the commercial glasses were determined by routine analysis. The compositions of the optical glasses were calculated from the batch composition except for the oxides of arsenic when values are given for both As_2O_5 and As_2O_3. In these cases the arsenic was determined analytically. The batch materials used in making the optical glasses were practically free from sulphur compounds.

[3] Not analyzed except for SO_3.

TABLE 2.—*Variation in individual determinations on light crown optical glass*

[All determinations made at 1,300° C and on samples from the same melt]

Weight of sample	Amounts of gases obtained			Blank		Gas per 100 g of glass		
	H_2O	O_2+R	CO_2	O_2+R	CO_2	H_2O as gas	O_2+R	[a] CO_2
g	g	ml	ml	ml	ml	ml	ml	ml
20.54	0.0057	0.38	1.21	0.18	0.02	34	1.0	5.8
24.09	.0067	.46	.92	.18	.04	35	1.2	3.7
21.34	.0042	.43	.66	.08	.03	25	1.6	3.0
22.50	.0068	.70	.83	.06	.02	38	2.8	3.6

[a] Since the amount of sulphate in the batch material from which this glass was made was very small, the gas absorbed by the Ascarite was considered to be entirely CO_2.

IV. EFFECT OF CONDENSED OXIDES

Table 2 gives the results of four separate determinations made at 1,300° C on light crown optical glass.

There is considerable variation in the amounts found of any given constituent, and this can be explained only as arising from the method used for vacuum fusion, since it is not reasonable to assume that there was a significant difference in the glass itself as the samples were all taken from the same large piece. The chief source of error is undoubtedly the absorption of the evolved gases by the volatilized oxides (such as those of sodium, boron, etc.) which condense on the colder portions of the vacuum furnace. Indeed, it seems that this absorption is so important that it outweighs any other sources of error that might exist. In all the determinations that were made the presence of condensed oxides was observed.

To determine how much absorption takes place under extremely adverse conditions, two determinations were made on a soda-lime-silica glass, the first portion of the sample being completely outgassed before the second portion was added. The furnace and crucible were not cleaned between the first and second heatings. In order that the water-absorption tube might be removed for weighing the water from the first portion of the sample, dry air was admitted to the furnace. This made it necessary to degas the furnace again. The first portion of the glass was, therefore, heated in the crucible for a total of 2 hours before the second portion of the sample was added. Since, under these conditions, no measurable quantity of gas was obtained from the second portion, the gas evolved must have been entirely absorbed by the condensed oxides volatilized during the first part of the test.

TABLE 3.—*Effect of condensed oxides on amounts of gases obtained from soda-lime tubing glass*

Sample [1]	Weight of glass	H_2O	O_2+R	CO_2	Gas per 100 g of glass		
					H_2O	O_2+R	CO_2
	g	ml	ml	ml	ml	ml	ml
A_1	7.11	2.0	0.04	0.62	28	0.6	8.7
A_2	5.62	0	----------	0	0	0	0
B_1	8.28	1.7	.07	1.13	21	.8	13.7
B_2	6.50	0	----------	0	0	0	0

[1] A_1 and A_2 and also B_1 and B_2 are the first and second portions, respectively, of the sample used in 1 determination.

These data are given in table 3 and indicate that in any series of determinations on one glass even the highest values obtained may be far too low. The amount of absorption by condensed oxides will depend, among other things, on the composition of the glass, the temperature at which the vacuum fusion takes place, the rate at which the gases are removed from the furnace, and the shape and volume of the furnace.

V. EFFECT OF STIRRING AND FINING TIME

In table 4 are given the results obtained on samples taken from pots of optical glass at intervals during the stirring and fining periods. The total time taken for stirring [9] the glass and the time and temperature at which the melt was sampled are indicated.

There was apparently no significant change in the gas content after the batch was completely melted and stirring had been started, the carbon dioxide and oxygen being entirely eliminated, or nearly so, and the water content reaching a constant value during the early stages of the melt. Since the optical glass had been vigorously stirred, it was to be expected that an equilibrium between the carbon dioxide and water in the glass and in the furnace atmosphere would be reached more rapidly than when the glass is not stirred, as in ordinary commercial practice. The stirring may also explain why we found much less oxygen in the light crown optical glass containing arsenic than Dalton [10] found in a glass of similar composition.

TABLE 4.—*Gases obtained from samples of optical glass taken at various times during the melting period*

Temperature of melt when sample was taken.	Time between start of stirring and taking of sample for test.	Gas per 100 g of glass		
		H_2O	O_2+R	CO_2
°C	hr	ml	ml	ml
1,400	1.5	45	0	0
1,400	3.0	28	0	0
1,275	7.5	32	0	0
1,275	11.5	34	0	0
(a)	b 14.0	29	0	0
LIGHT BARIUM CROWN GLASS *C*				
1,360	7.0	15	2.7	0
1,360	9.0	23	2.0	0
1,295	12.5	17	2.5	0.3
(a)	b 16.0	17	1.1	<.1
LIGHT CROWN GLASS *B*				
1,410	1.0	28	6.0	3.0
1,410	4.0	35	5.4	3.0
1,375	8.0	33	6.9	2.2
1,350	12.0	29	5.5	5.1
(a)	b 13.0	38	5.4	4.1

[a] Finished glass. The sample for this test was taken after the glass had cooled.
[b] Indicates the time between the start of stirring and the removal of the pot from the furnace.

[9] Stirring was started about 1 hour after the last batch fill.
[10] R. H. Dalton. J. Am. Ceram. Soc. **16**, 425 (1933).

VI. SUMMARY AND CONCLUSIONS

An apparatus and procedure for extracting and measuring the gases obtained from molten glass are described. Measurements of dissolved gases were made on 14 glasses representing 3 types of optical glass and 7 commercial tank glasses. Water was the most abundant gas in the optical glasses, while the commercial tank glasses, all of which contained sulphur compounds, yielded appreciable quantities of "SO_2+CO_2" and "O_2+R" in addition to water in amounts comparable to that in the optical glasses. The total volume of gases extracted from the glass was from one-half to several times the volume of the glass itself.

The method used for extracting and measuring the gas has given only fairly reproducible results, and it is thought that all results are low because of absorption of the gases by the oxides from the glass that condense in the upper portion of the furnace. This absorption could probably be lowered by redesigning the apparatus in such a way that the gases could be more rapidly removed from the furnace.

Since the amount of gas obtained from all the optical glasses was relatively small in comparison with that obtained from window glass, and since all the glasses except the light barium crown were relatively free from seeds, there is probably no relation between dissolved gas and the prevalence of seeds in the light barium crown. Furthermore, there was no significant difference in the amounts of gases obtained from samples taken at intervals during the stirring and fining periods, although the seeds decreased materially in size and number during these periods.

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WICK TEST FOR EFFLORESCENCE OF BUILDING BRICK

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ABSTRACT

This paper describes the wick test for efflorescence on building bricks and presents data showing the relation between results of wick tests and the appearance of efflorescence on exposed masonry panels. It is concluded that the results of the 5-day wick test correlate well with the grading on exposed panels when the efflorescence on individual bricks rated in excess of "moderate" on the scale used for grading intensity of visible efflorescence.

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I. INTRODUCTION

If a brick is set on end in shallow water and that portion of the brick above the water is exposed to conditions favoring evaporation, water entering the brick by capillarity will move upward and outward through the brick. The water will tend to dissolve soluble salts in the brick and transport them to its surface where they may be progressively deposited as the water, in which they are dissolved, evaporates. These phenomena have been variously applied in a "wick test" which may be regarded as a test to indicate the presence of soluble salts which may contribute to efflorescence on masonry.

The authors of this report do not know who first used this test for efflorescence, but one of the authors tested brick by this method in 1922. Palmer [1] reported, "The brick were set vertically in the pan and in about 1 inch of distilled water, and the tests in all cases were continued for a period of 6 months." Butterworth [2] used a wick test with exposure from 2 to 3 weeks. In 1930, 5-day wick tests were made on 684 bricks, each of a different grade or brand, from 255 manufacturers. Although the results of these tests were not published they were given to the manufacturers supplying the samples. Since 1930 considerable use of the wick test has been made by the National Bureau of Standards at the request of certain Government construction agencies.

In the late summer of 1936 a number of small panels or wallettes were constructed from 18 types of brick for the purpose of studying the effects of weather on brick masonry, including efflorescence. Samples of the brick used in constructing these panels were subjected

[1] BS Tech Pap. 22, 584 (1928) T370.
[2] B. Butterworth, *Contributions to the study of florescences*, Trans. Ceram. Soc. 32, 270 (1933).

to the 5-day wick test. The relation between the results of this wick test on the brick and the amount of apparent efflorescence on these panels is considered in this paper.

II. WICK TEST FOR EFFLORESCENCE

At the National Bureau of Standards, the wick test consists in standing a whole brick on end in 0.5 inch of distilled water, maintained at approximately a constant level by inverting a flask of water over the tray, with the mouth of the flask held at the desired level. The brick, except that portion in contact with water, is exposed to the air of the laboratory at ordinary temperature. At the end of 5 days the brick is dried in an oven at 105° to 110° C for at least 18 hr, and the amount of efflorescence is estimated by visual comparison with an untreated specimen.

The amount of efflorescence is rated on a scale consisting of six classifications or grades, described as follows:

None (0).—No observable difference in the appearances of a brick after test and before.

Trace (1).—Efflorescence barely distinguishable by careful comparison.

Slight (2).—Observable. Not sufficient efflorescence to materially affect the appearance when viewed at a distance of approximately 6 feet.

Moderate (3).—Distinct coating, but the original color of the brick distinguishable under the efflorescence.

Considerable (4).—The original color of the brick masked by the efflorescence.

Abundant (5).—Efflorescence in such quantity that it may be brushed off readily.

It is considered that Butterworth's [3] first grade, "bricks that are not liable to efflorescence, i. e., those on which the efflorescence developed in the test is nil or negligible", corresponds to the "none", "trace", and "slight" of this grading. His second grade, "bricks that can only be recommended with reserve from the point of view of efflorescence", represents "moderate" and possibly "considerable", and the third grade, "bricks the use of which would constitute a disaster", corresponds to "abundant."

In the wick test on a particular brick, the amount of efflorescence that appears on the surface is affected by several factors other than the quantity of salts per unit of volume of the brick.[4] For example, if the brick has a very low rate of absorption, approximate equilibrium will be quickly reached between water evaporated and water diffusing through the brick by capillarity. Efflorescence will, under these conditions, appear at the junction between the damp and dry portions of the brick, usually as a horizontal band around the brick. On one specimen, this band was less than 1 inch above the surface of the water. Obviously, the dry portion of this brick did not contribute to the efflorescence. Again, there are certain combinations of temperature, humidity, circulation of air, and pore structure in which evaporation will take place beneath the surface of the brick with the result that some salts will be deposited there and hence will not be

[3] See footnote 2.

[4] If standardization of the wick test is to be attempted, one might begin by prescribing the temperature, humidity, and velocity of air and then working either for a definite time or until a definite quantity of water has been evaporated.

visible. This is the "cryptoflorescence" referred to by Cooling.[5] Then, too, if the brick specimen has a large total absorption, a high rate of absorption, and contains a moderate amount of readily soluble salts, the efflorescence obtained in the wick test may appear as beads on the four upper corners of the brick instead of being distributed over the surface.

III. EXPOSURE TESTS OF PANELS OF BRICK MASONRY

The panels considered in this study of the relations between the results of the wick test and the actual exposures were made of 18 brands of brick (briefly described in table 1) and a single kind of mortar (1.0 portland cement:0.1 hydrated lime:3.0 sand, by weight). All panels are 4 feet high, 3 feet long, and 12 inches thick, and they are set vertically 12 inches deep in the ground. Common bond was used throughout and the workmanship was characterized by furrowing of the horizontal joints and a minimum filling of the vertical joints.

TABLE 1.—*Comparison of results of 5-day wick tests for efflorescence of brick and efflorescence ratings for masonry panels*

Brick	Wick-test ratings [a]	Ratings for masonry panels [a]								Absorption data [b]		Description of bricks [c]
		First inspection of panels with protection				Second inspection of panels with protection						
		a	*b*	*c*	*d*	*a*	*b*	*c*	*d*	*C/B*	*B*	
											(%)	
1	0	4	3	3	3	2	2	2	2	0.69	24	*SM; C;* salmon, Pennsylvania.
2	0	1	2	2	0	1	2	1	1	.81	15	*DP; C;* Virginia.
3	0	1	1	0	2	1	1	1	1	.71	18	Sandlime, Pennsylvania.
4	0	2	1	3	2	1	1	1	1	.71	12	*SC; C;* Maryland.
5	1	4	3	3	[d] 1	2	2	2	2	.74	17	*SM; C;* hard, Pennsylvania.
6	1	2	1	2	1	3	3	3	3	.75	15	*EC; C;* Chicago.
7	2	3	4	3	3	4	3	3	3	.87	24	*SM; C;* Detroit.
8	2	3	4	3	4	3	2	1	3	.91	33	*SC; C;* Wisconsin.
9	3	0	1	1	1	2	1	2	2	.86	14	*SC; S;* light hard, West Virginia.
10	4	4	3	3	1	4	3	4	3	.88	14	*DP; S;* Texas.
11	4	4	4	4	3	4	4	4	3	.83	21	*SM; C;* hard, Hudson Valley.
12	4	5	4	4	4	3	4	3	3	.90	23	*SM; C;* salmon, Hudson Valley.
13	4	5	4	5	4	3	3	3	3	.84	18	*SM; C;* salmon, New England.
14	4	4	----	----	----	4	----	----	----	.86	11	*SC; S;* deaired, Pennsylvania.
15	0 to 2	0	1	2	0	2	2	2	1	.57	5	*SC; S;* hard, West Virginia.
16	0 to 5	[e] 2	[f] 1	3	0	3	2	3	2	.64	16	*SC; S;* Minnesota.
17	1 to 3	3	2	2	2	2	1	2	1	.78	33	*DP; C;* Texas.
18	2 to 3	1	1	2	2	2	2	2	1	.84	12	*SC; C;* salmon, Maryland.

[a] For convenience, the ratings are expressed numerically, as follows: 0, none; 1, trace; 2, slight; 3, moderate; 4, considerable; 5, abundant.

[b] *C*, water absorption in the 24-hour submersion test, and *B*, water absorption in the 5-hour boiling test, described in the Tentative Methods for Testing Brick (ASTM designation C 67-36T), Proc. Am. Soc. Testing Materials **36**, I, 780 (1936).

[c] *SM*, soft mud; *SC*, side cut; *EC*, end cut; *DP*, dry press; *C*, clay; *S*, shale.

[d] 2 bricks rated 3.

[e] 1 brick rated 4.

Each brand of brick (except 14) was used to build four panels, each of which was "protected" differently, as follows:

a No protection.

[5] L. F. Cooling, *Contributions to the study of florescence.* II. *Evaporation of water from brick*, Trans. Ceram. Soc. **29**, 39-52 (1930).

b Top of panel covered with loosely fitting sheet-copper cap.

c Sheet-copper "flashing" in horizontal joint through the panel, 2 inches above ground level.

d Combination of *b* and *c*. (See fig. 1.)

The panels are placed on top of a gradually sloping and somewhat wooded knoll in the northwest corner of the Bureau's grounds at Washington, D. C. This site was selected so that all panels would be exposed to essentially the same atmospheric conditions. The individual panels, facing east and west, were spaced 5 feet apart between faces and 4 inches apart between ends.

Random samples consisting of 12 specimens each of the 18 brands of brick used in the construction of these panels were subjected to the 5-day wick test.

IV. RELATION BETWEEN INDICATIONS OF WICK TESTS ON BRICK AND EFFLORESCENCE ON EXPOSED MASONRY PANELS

The masonry panels were inspected on November 30, 1936 and again on March 4, 1937. The first inspection was made 6 weeks after completion of construction of the panels. There had been no rain for 2 weeks preceding this inspection. Subsequent rains temporarily removed all traces of visible salts from the panels. The second inspection took place on the fourth day of clear weather.

The selection of the ratings for efflorescence on the panels was not as simple as for individual bricks, because the ratings assigned to the panels depended to a far greater extent upon the judgment of the inspector. Both intensity and distribution of the efflorescence were considered. As indicated by footnotes in table 1, some of the bricks in certain panels of bricks 5 and 16 showed much more efflorescence than others during the first inspection. At the time of the second inspection, the efflorescence was more uniformly distributed. In attempting to evaluate or visualize the appearance of the panels it might be stated that ratings less than "moderate" (3) indicate no material change in the appearance of masonry when viewed from a distance of 20 feet.

Table 1 includes the results of the wick tests, the results of these two inspections, and data on the absorption of the bricks. The reader is cautioned against ascribing any cardinal significance to the numerals used in rating efflorescence. It is probable that the difference in the amounts of salts warranting a change of rating from "moderate" (3) to "considerable" (4) was greater than the difference to change from "none" (0) to "moderate" (3).

The data pertaining to bricks 1 to 14, inclusive, are grouped according to the ratings for these bricks in the wick test. The individual bricks (12 each) of each of these types were rated alike in that test. Those for bricks 15 to 18, inclusive, showed significantly different amounts of efflorescence in the wick test, and the data for these are in a separate group.

The data of table 1 pertaining to bricks 1 to 14, inclusive, show the following:

1. When the rating of the bricks in the wick test was "considerable" (4), 16 of the 17 panels built from these bricks rated "moderate" (3) or more in the first inspection, and all of these rated "moderate" (3) or more in the second inspection.

FIGURE 1.—*Panel of brick, 2 showing sheet-copper cap over top and sheet-copper flashing above ground (protection d).*

(Photograph taken Nov. 25, 1936.)

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2. When the rating of the bricks was "slight" (2) or less, 27 of the 32 panels of the bricks rated "moderate" (3) or less in the first inspection, and 31 of the 32 rated "moderate" (3) or less in the second inspection.

3. When the rating of the bricks was "trace" (1) or less, 22 of the 24 panels rated "moderate" (3) or less in the first inspection, and in the second inspection all rated "moderate" (3) or less and 20 of the 24 rated "slight" (2) or less.

4. The data presented do not show that the kind of protection had a significant effect on the amount of efflorescence on the panels.

It is evident that the correlation between the indications of the wick tests on the bricks and the appearance on efflorescence of the masonry was somewhat better for the data of the second than for the first inspection. Possibly data obtained during future inspections will show a continuance of this trend and also a significant difference in the appearance of panels with different protections (*b*, *c*, *d*).

The panels built with bricks rating "none" (0) to "slight" (2) tended to rate one or two grades higher than the individual bricks. Some of the efflorescence on these panels probably was caused by soluble salts originally in the mortar. The appearance of the panels during the first inspection indicated that salts from the mortar had contributed to the deposit. The efflorescence on most of the panels appeared on the exposed faces of the bricks and was chalk white in color; whereas, that on some of the panels of bricks rating "none" (0) was limited largely to the joints and edges of the bricks adjacent thereto and was gray in color.

V. SUMMARY AND CONCLUSIONS

The paper describes the wick test used at the National Bureau of Standards for indicating the tendency of bricks to be a source of efflorescence on masonry and outlines the scale of grading used in reporting and comparing the results. Comparisons are made between the performance of bricks in the test and the appearance of efflorescence on brick masonry exposed to the weather at Washington, D. C.

The results of the tests and comparisons showed that—

1. If considerable efflorescence appeared on bricks in the 5-day wick test, masonry panels built of bricks of the same brand showed an objectionable (moderate or more) amount of efflorescence.

2. If the efflorescence on bricks in the wick test was only a trace or less most of the masonry panels built from the same brand of bricks showed only a slight (or less) amount of efflorescence.

3. Soluble salts from mortar appeared to have caused efflorescence on some of the panels.

WASHINGTON, MAY 14, 1937.

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